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Investigation of Separation, Treatment, and Recycling Options for Hazardous Paint Blast Media Waste

by

Jeffrey H. Boy, Timothy D. Race, and Keturah A. Reinbold

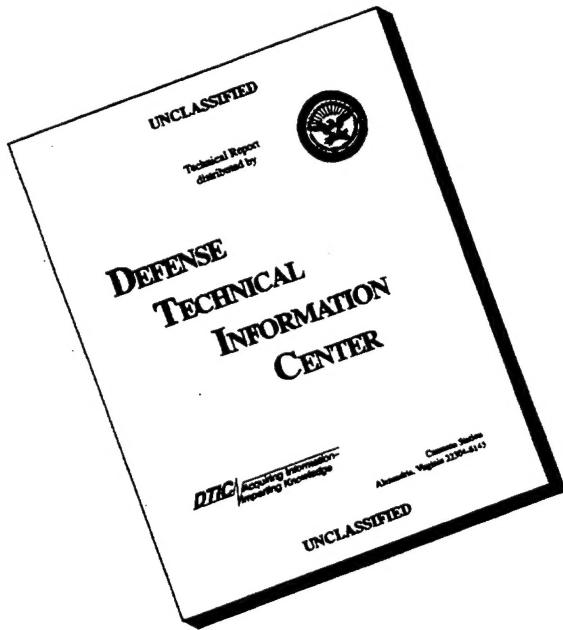
U.S. Army depot depaint operations generate over 4 million kg per year of contaminated paint blast media wastes. A variety of abrasive blast media are used. Spent blast media wastes are often determined to be hazardous when tested for characteristic metals using Toxicity Characteristic Leaching Procedure (TCLP) Method 1311. Disposal of contaminated blast media is regulated by the Environmental Protection Agency as well as state and local authorities. Because environmentally sound disposal of hazardous waste is very expensive, the Army could significantly benefit from cost-effective treatment processes that would render paint blast media wastes nonhazardous, or reduce waste bulk by isolating and disposing separately of hazardous components. The objective of this work was to investigate technologies that might significantly mitigate this Army hazardous waste disposal problem.

Most of the technologies investigated either failed to meet acceptable TCLP levels for hazardous metals content, or failed to meet Army disposal requirements. However, based on a review of several commercially available services, it is recommended that Army depot depaint operations consider processing hazardous blast media waste through properly regulated contractors that offer safe, effective, and economical stabilization, fixation, and recycling technologies. Due consideration should include an appropriate legal review of liability and regulatory issues.

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Foreword

This research was performed for the U.S. Army Environmental Center under Project 4A262720D048, "Industrial Operations Pollution Control Technology"; Work Unit NN-UT4, "Hazardous Waste Separation from Paint Blast Media." The technical monitor was Ronald P. Jackson, ENAEC-TS-D.

The work was performed by the Materials Science and Technology Division (FL-M) of the Facilities Technology Laboratory (FL), and the Natural Resources Assessment and Management Division (LL-N) of the Land Management Laboratory (LL), U.S. Army Construction Engineering Research Laboratories (USACERL). Dr. Alan W. Moore is Acting Chief and Donald F. Fournier is Acting Operations Chief, CECER-FL. William D. Goran is Chief and Dr. William D. Severinghaus is Acting Operations Chief, CECER-LL.

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COL James T. Scott is Commander and Acting Director of USACERL, and Dr. Michael J. O'Connor is Technical Director.

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1 Introduction

Background

Abrasive blasting has become the preferred method of paint removal at Army maintenance facilities (PEI 1990). Army facilities generate over 4 million kg per year of contaminated paint blast media wastes from paint removal operations. Depending on the paint system and substrate, a variety of abrasive blast media may be used for paint removal. Most blasting operations have a recirculation system that removes spent blast media particles too small for efficient paint removal. The resulting blast media wastes are often determined to be hazardous when tested for characteristic metals using the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) Method 1311. The typical contaminants found in spent media are barium, cadmium, chromium, and lead. Disposal of contaminated blast media is regulated by the Federal government through, for example, the *Resource Conservation and Recovery Act of 1976* (RCRA, PL 94-580, as amended) as well as by state and local authorities. Because environmentally sound disposal of hazardous waste is very expensive, the Army could significantly benefit from cost-effective treatment processes that would render paint blast media waste nonhazardous, or reduce waste bulk by isolating and disposing separately of hazardous components. The U.S. Army Construction Engineering Research Laboratories (USACERL) was tasked to investigate technologies that might significantly mitigate this hazardous waste disposal problem.

Objective

The objective of this work was to evaluate and identify cost-effective processes for separating, breaking down, immobilizing, or recycling hazardous compounds in paint blast media wastes generated by Army depot depaint operations.

Approach

The Air Force Engineering and Service Laboratories previously evaluated disposal and recovery methods for plastic media blasting (PMB) waste in a multiphase research

program. The results of these studies (Tapscott, Blahut, and Kellogg 1988; Jermyn and Wichner 1991) were reviewed by the researchers to avoid duplication of effort and to eliminate previously evaluated and rejected technologies.

Personnel from the U.S. Army Construction Engineering Research Laboratories (USACERL) conducted site visits to Army maintenance facilities where abrasive paint blast operations were performed. These included Red River Army Depot, TX; Sacramento Army Depot, CA; Corpus Christi Army Depot, TX; Tooele Army Depot, UT; Anniston Army Depot, AL; and Letterkenny Army Depot, PA. USACERL personnel observed these operations and retrieved samples of blast media waste for laboratory analysis and testing.

Waste processing techniques investigated in the laboratory by USACERL included cement stabilization and acid digestion. USACERL personnel also evaluated the chemical stabilization and fixation processes used by Red River Army Depot, and performed independent laboratory tests to verify the suitability of the process. Additional studies were performed by contractors to investigate microbiological digestion and low-temperature ashing (incineration). USACERL personnel also visited Army and Air Force maintenance facilities using lease recycle programs, and evaluated those programs.

Mode of Technology Transfer

The technologies recommended in this report may be suitable for use by a variety of Department of Defense installations including all Army, Navy, Air Force, Marine, Corps and National Guard installations involved in the repair and renovation of equipment. Technology transfer will be through the U.S. Army Environmental Center (USAEC) and the Army Center for Technical Excellence (CTX) for Mechanical Depaint (Industrial Operations Command), Anniston Army Depot, AL. The findings of this research were presented and published in the technical proceedings of the following symposia: the 17th Army Environmental Research and Development Conference (Boy et al., June 1993), the American Ceramic Society annual meeting (Bukowski et al., April 1994), and the 87th Annual Air and Waste Management Conference (Boy et al., June 1994). Results were also published in the peer-reviewed journal *Hazardous Waste & Hazardous Materials* (Boy et al. 1995).

Units of Measure

This report principally uses standard international (SI) units of measure. Where any U.S. standard unit appears, a conversion factor is provided on first use.

2 Abrasive Blasting Processes, Media, and Waste

Selection of Abrasive

Selection of the size and type of abrasive that most effectively and economically produces the desired surface finish depends on several variables including:

- the nature of the substrate being cleaned, including surface hardness
- the degree of corrosion that may have developed before blast cleaning
- the nature of any previous paint or coating system
- the type of surface finish desired.

Steel shot is a common abrasive blast media used on heavy steel structures. Steel shot consists of spherical particles of steel created by granulating a molten stream of metal with water, air, or other methods. Cast steel grit consist of angular particles produced by crushing steel shot.

Nonmetallic abrasive blast media are listed in Table 1*. Sand has been replaced by a number of alternatives because of the respiratory hazards associated with free silica. Inorganic substitutes in use are garnet, alumina (aluminum oxide), silicon carbide, and glass beads. Agricultural media include ground walnut shells or apricot pits, and wheat starch or corn starch products.

A number of plastic blast media available for paint removal are summarized in Table 2. The harder and larger particles generally provide faster paint removal but are also more likely to damage to the underlying substrate. Therefore, on sensitive equipment, softer materials (with slower removal rates) are often used.

The types and distribution of media used at two Army maintenance facilities are shown in Table 3. The wide variety of abrasive blast media used at various Army maintenance facilities makes it difficult to develop one optimum waste separation technique for universal Army use.

* Tables and figures in this report may be found at the end of the chapter in which they are first referenced.

Substrate Considerations

Grey (1993) reviewed the advantages and disadvantages for the use of plastic blast media. Although paint removal from hard steel substrates, used in support equipment, proved to be very successful by plastic media blasting (PMB), it did not produce the surface roughness that normally occurred with grit blasting. A more aggressive blast media such as steel shot or mineral abrasives will produce the appropriate roughness.

Clad-type aluminum alloys are often used in structures exposed to severe environments such as those found in many military aircraft components. This clad aluminum consists of a corrosion-prone structural aluminum core with an outer cladding layer of a more corrosion-resistant aluminum alloy. Because this outer layer is soft, it is prone to damage during paint removal. The use of Type V acrylic plastic media has been found to inflict less damage to this outer layer than Type II urea formaldehyde plastic media (Grey 1993; Pauli 1993).

Paint removal from composites during maintenance has generally been difficult. Grey (1993) reported that Type V acrylic media or specialized commercial media (Type VI) may be used with operating conditions that remove minimal amounts of the polymer matrix. Alternately, the use of wheat starch for paint removal on air frames, has been accepted by several major aerospace manufacturers. The use of agricultural and starch abrasive media continues to grow (Pauli 1993). A variety of agricultural based abrasive blast media have been approved for use by the military (Military Specification [Mil] G-634C), Table 4.

Waste Characterization

Waste treatment technologies for PMB waste have been previously evaluated by the U.S. Air Force Engineering and Services Center and Oak Ridge National Laboratory (Tapscott, Blahut, and Kellogg 1988; Jermyn and Wichner 1991). Paint blast media waste is generated by in-line classification equipment that rejects all material passing through a 60 mesh screen. This corresponds to particles smaller than 250 μm . Size measurements performed by sieving indicated a highly variable particle size distribution, generally between 38 and 250 μm . However, photomicrographs revealed many particles of a much smaller size, ranging between 1.0 and 0.1 μm . In addition, they reported that photomicrographs showed numerous extremely small particles, which they attributed to the stripped paint, that were adhered to the large degraded PMB particles. They further concluded that dry separation treatments which seek to reduce waste volume by removing the paint particle from the degraded PMB waste would

likely be ineffective due to the adhesive forces between the small paint particles and the larger blast media particles.

Toxic Characteristic Leaching Procedure

The Toxicity Characteristic Leaching Procedure (TCLP) is the means mandated by the EPA for determining the toxicity of a hazardous material (Federal Register, 13 June 1986). Method 1311, the procedure used in this research, is outlined below:

1. A 100 gram sample of the waste is crushed to pass through a 9.5 mm standard sieve
2. A 5 gm portion of the sample is used to determine the extraction solution
 - A 5 gm sample is weighed into a 250 ml beaker
 - 99.5 ml of deionized water is added to the 5 gm sample, stirred vigorously for 5 minutes, and the pH of the solution is determined
 - If the pH is <5.0, then Extraction Solution A is used—an acetic acid-sodium acetate buffer solution (pH = 4.93 +/- 0.05)
 - If the pH is >5.0, then Extraction Solution B is used—an acetic acid solution (pH = 3.88 +/- 0.05). (Note: this is the only point at which the pH is determined in the TCLP.)
3. A 100 gram sample is transferred to a plastic bottle and 2 liters of the appropriate extraction solution is added.
4. The sample is rotated for 18 +/- 2 hours.
5. The sample is filtered and the extraction fluid retained for chemical analysis.

Chemical Analysis

As part of this study, USACERL personnel retrieved samples of paint blast media waste from operations at several Army depots. The results of the laboratory testing and analysis are presented in Appendix A, Tables A1-A10.

The principal RCRA metal contaminants in paint blast media waste were found to be barium (Ba), cadmium (Cd), chromium (Cr), and lead (Pb). The blast media waste samples failed the TCLP extraction test for Cd, Cr, and Pb. No sample failed TCLP for Ba. The principal difficulties of this work were: (1) the wide variety of blast media types utilized at the various facilities (see Table 3) and (2) the wide variability of contaminant concentration for a given waste from any individual facility. This variability arose from the diversity of waste, sources, and paint systems being removed at the time of waste sampling.

Table 1. Physical data on nonmetallic abrasives.

Media	Hardness (Mohs)		Sp. Gr.	Bulk Density (g/ml)		Fee Silica	Degree of Dusting Reuse	
	Shape	Color						
Naturally Occurring Abrasives								
Silica								
Silica	5	Round	2 to 3	100	White	90 +	High	Poor
Mineral	5 to 7	Round	3 to 4	125	Variable	< 5	Medium	Good
Flint	6.7 to 7	Angular	2 to 3	80	Lt. Gray	90 +	Medium	Good
Garnet	7.5	Angular	4	145	Pink	nil	Medium	Good
Zircon	47.5	Cubic	4.5	185	White	nil	Low	Good
Novaculite	4	Angular	2.5	100	White	90 +	Low	Good
By-Product Abrasives								
Slags								
Boiler	7	Angular	2.8	85	Black	nil	High	Poor
Copper	8	Angular	3.3	110	Black	nil	Low	Good
Nickel	8	Angular	2.7	85	Black	nil	High	Poor
Walnut Shells	3	Cubic	1.3	45	Black	nil	Low	Poor
Peach Shells	3	Cubic	1.3	45	Black	nil	Low	Poor
Corn Cobs	3	Angular	1.3	45	Black	nil	Low	Good
Manufactured Abrasives								
Silicon Carbide	9	Angular	3.2	105	Black	nil	Low	Good
Aluminum Oxide	8	Blocky	4.0	120	Black	nil	Low	Good
Glass Beads	5.5	Spherical	2.5	100	Black	nil	Low	Good

Source: From SSPC's *Steel Structures Painting Manual, Volume Two, Systems and Specifications*, 6th Edition ©1991. Used with permission of the Steel Structures Painting Council (SSPC), 40 24th Street, 6th Floor, Pittsburgh, Pennsylvania 15222-4643, USA.

Table 2. Comparative properties of plastic media used in paint stripping.

Type	Composition	Thermal Properties	Hardness (Barcol)	Paint Stripping Rate	Effect On Substrate	Applications
I	Polyester	Thermoset	34 to 42	Slow	Low	Thin sections metal Alloys
II	Urea Formaldehyde	Thermoset	54 to 62	Acceptable	Medium	Non-critical thin section metal alloy
III	Melamine-Formaldehyde	Thermoset	64 to 74	Fast	Severe	Steel and other ferrous alloys
IV	Phenol-Formaldehyde	Thermoset	54 to 62	Fast	Very Severe	Steel and other ferrous alloys
V	Acrylic	Thermo-plastic	46 to 54	Acceptable	Low	Thin section metal alloys & composites
VI	Poly-allyl-diglycol-carbonate	Thermo-plastic	20 to 30	Acceptable	Very Low	Thin section metal alloys & composites

Source: Grey 1993.

Table 3. Summary of abrasive paint operations at selected Army depots.

Media	Anniston		Letterkenny	
	10 ³ Kg	%	10 ³ Kg	%
Walnut Shells	240	15	1306	80
Coal Slags	827	51		
Magnesium/Iron Silicates	400	24		
Plastic Media			82	5
Glass	80	5	26	1
Aluminum Oxide	40	2.5		
Steel Shot	40	2.5	226	14
Sand			5	>1
Totals	1627	100	1645	100

Source: PEI 1990.

Table 4. Grain, abrasive, soft, for carbon removal.

Type	Media	Approved Use
I	Apricot Pits	Aircraft jet engine or general purpose use
II	Pecan Shells	General purpose use only
III	Black Walnut Shells	Aircraft jet engine or general purpose use
IV	Corn Cobs	General purpose use only
IV	Rice Hulls	General purpose use only
VI	English walnut shells, apricot pit shells, or a mixture of the two	Aircraft jet engines only
VII	Peach Pits	Aircraft jet engines or general purpose use

Source: Military Specification (MIL) G-5634C.

3 Physical Separation Processes for PMB

The Air Force Engineering and Service Laboratories (Tapscott, Blahut, and Kellogg 1988) evaluated cost-effective and environmentally sound disposal and recovery methods for PMB waste residues. The physical, chemical, and thermal treatment processes evaluated are summarized in Table 5. The knowledge gained in this and subsequent work was used to avoid duplication of effort by USACERL and to eliminate previously evaluated and rejected technologies.

Dry Separation Processes

Waste samples were separated into various particle size fractions using a series of progressively finer sieves. Tapscott, Blahut, and Kellogg (1988) concluded that because the hazardous and nonhazardous particulate are very close in size, screening cannot efficiently separate the waste into regulated and nonregulated components.

Electrostatic separation was also evaluated in the Air Force study. Electrostatic separation involved injecting the PMB waste into a high-voltage direct-current electrical field. After exposure to the electric field, material falls to either side of a gate: material more attracted to the electric field falls to one side of the gate and material less attracted falls to the other side of the gate. Tapscott, Blahut, and Kellogg (1988) reported that the process sometimes resulted in fractions that differed greatly in metal concentrations, but the results were erratic and separation was insufficient.

Liquid Media Separation

Tapscott, Blahut, and Kellogg (1988) evaluated liquid density separation as a means to separate PMB waste into metals-rich and metals-depleted fractions. A ferric chloride solution showed little separation while potassium iodine solution showed modest success in generating a float-rich fraction. Carbon tetrachloride (CCl_4) worked very well, giving sink materials containing most of the metal contaminants. However, owing to the cost and toxicity of this material, handling and disposal would be difficult and expensive. A separation was also attempted with the less toxic chlorofluorocarbon (CFC) 113 ($CF_2ClCFCl_2$). The analysis showed little separation.

Additional work was performed on the liquid density separation of the hazardous component from PMB waste as summarized in Table 7 (Jermyn and Wichner 1991). Visual evidence indicated good physical separation of Type V PMB and paint solids using a potassium carbonate (K_2CO_3) solution with a density of 1.30 g/ml. Agitation (ultrasonic vibration and pumped circulation stirring) and centrifugation were found to aid physical separation. Addition of a surfactant (Turgitol) had only a marginal effect. Potassium carbonate solution had a deleterious chemical effect as lead and chromium leached into the liquid. Lead and barium were found to be more leachable by means of TCLP as the paint solids deteriorated. Calcium bromide solution (1.3 g/ml) also yielded good physical separation of Type V PMB and paint solids. Yellow coloration of the liquid occurred, indicating the presence of chromium in solution. However, calcium bromide solution (1.60 g/ml) yielded good physical separation of Type V PMB and paint solids. No liquid coloration occurred. Sucrose solutions (density 1.25) yielded poor separation. The researchers found that liquid density separation generally resulted in significant leaching of the metal contaminants into the liquid solution so the liquid itself was rendered a characteristic hazardous material.

Conclusions on the feasibility of liquid media separation (Jermyn and Wichner, 1991) included the following:

- The possibility of leaching pigment metals (particularly chromium) into solution, detracts from the liquid media separation concept
- Some water-based liquids render the pigment metals more susceptible to TCLP extraction; in some cases marginally hazardous PMB waste becomes more hazardous
- It would be difficult to develop a liquid media separation process for a broad range of paint and PMB densities that would provide effective separation and not leach metals
- Since there appeared to be no suitable organic liquid for such a process, the concept of liquid media density separation of PMB paint solids should not be further pursued.

Table 5. Results of Air Force survey of waste treatment options.

Treatment Method	Positive	Negative	Recommendations
Incineration	High degree of volume reduction	Regulatory difficulty, costly, hazardous off gasses	Not recommended
Chemical treatment		Produces hazardous liquid wastes	
Charring	Good waste reduction	Produces flammable off gas, regulatory difficulty	
Encapsulation in plastic	Passed EP toxicity test	High cost	
Encapsulation in cement	Passed EP toxicity test	Adds to waste volume, good formulation not found	
Density Separation*	Good waste reduction	Only hazardous liquids (CCl ₄ worked)	Recommended Best Approach
Electrostatic precipitation		Erratic results	
Aerodynamic classification		Poor waste concentration	

Source: Tapscott, Blahut, and Kellogg 1988.

Table 6. Metal ion analysis on density separated fractions.

	Fraction % of Total	Total Metals			EP Toxicity Test		
		Pb (ppm)	Cd (ppm)	Cr (ppm)	Pb (mg/L)	Cd (mg/L)	Cr (mg/L)
Ferric Chloride							
Float		400	200	380			
Sink		350	608	434			
Potassium Iodide Soln.							
Input		590	67	625	<0.2	1.08	18.0
Float	82%	590	67	625	<0.2	0.38	0.5
Sink	18%	230	25	150			
Carbon Tetrachloride							
Input		1400	60	1200	0.14	0.006	0.12
Float	94%	140	40	140	0.014	0.004	0.014
Sink	6%	17200	400	17100	1.72	0.040	1.71
CFC - 113							
Input		790	152	1700	<0.2	1.70	28.1
Float	28%	1390	248	2430	<0.2	1.97	64
Middle	16%	885	131	1480	<0.2	1.00	23
Sink	57%	660	191	1190	<0.2	10.4	20.5

Source: Tapscott, Blahut, and Kellogg 1988.

Table 7. Liquid density separation test.

PMB Waste	Liquid Solution	Liquid Density (g/ml)	Details	Results
Type V	Sucrose	1.25	Centrifuge (~500 G) ^a	No separation (with or without wetting agent)
Type V	Potassium Carbonate	<1.25	Centrifuge (~550 G)	No separation (with or without wetting agent)
Type V	Potassium carbonate	1.30	Centrifuge (~550 G)	Good separation (with or without wetting agent) Liquid colored yellow ^b
Type V	Potassium carbonate	1.30	1 Gravity settling, ultrasonic vibration and pumped circulation trials	Good separation (no wetting agent) Liquid colored yellow ^b
Type V	Calcium Bromide	1.30	1 Gravity settling, ultrasonic vibration and pumped circulation trials	Good separation (no wetting agent) Liquid colored yellow ^b
Type II	Calcium Bromide	1.30	1 Gravity Settling	Good separation Clear Liquid

Source: Jermyn and Wichner 1991.

^aIndicates acceleration in terms of gravity units^bIndicates extraction of chromium.

4 Low-Temperature Ashing

Objective of the Technology

Low-temperature ashing (LTA) involves subjecting the blast media waste to mild oxidation conditions at moderately elevated temperatures. Preliminary work was performed by Oak Ridge National Laboratory (ORNL) on LTA for the treatment of hazardous plastic blast media waste for the Air Force Engineering and Service Center (Jermyn and Wichner 1991). Weight loss measurements of a sample of Type V acrylic blast media heated to 500 °C in air resulted in a 95 percent reduction of the sample mass. The potential advantages of LTA includes a high degree of waste volume reduction. The ashing procedure reduces the waste volume down to the nonoxidizable portion of the waste (i.e., the pigment and the contaminants) and removes by vaporization the nonhazardous plastic portion that comprises at least 90 percent of the waste. The LTA treatment process is relatively robust. It does not depend on the microscopic properties of the waste (such as particle size) or pigment nature. Compared to high temperature incineration, LTA would be more likely to contain the hazardous components more completely within the ash than in the off-gas. The ash product of LTA would require further treatment before disposal. However the LTA ash to be disposed would be reduced to 5 percent of its original mass.

LTA Applicability and Process

LTA would be an appropriate candidate for treatment of blast media wastes that undergo significant decomposition upon heating in the temperature range of 500-600 °C. LTA would not be suitable for mineral or slag abrasives that have significantly higher melting points, nor for glass beads that melt without significant decomposition or volume reduction. In addition to Type V (acrylic) and Type III (urea formaldehyde) plastic media, LTA was investigated as possible treatment process for ground walnut shell blast media.

The experimental work, performed by ORNL, focused on determining certain thermal properties of virgin paint blast media used at Army maintenance facilities. The experiment involved three principal tests: (1) thermogravimetric (TG) analysis, i.e., weight loss as function of temperature at a controlled heating rate, (2) measurement

of the vaporized gas volume, and (3) characterization of significant volatile organic compounds (VOCs) generated during LTA. The objective was to test the suitability of LTA process against Army requirements. The procedures used by ORNL in conducting these tests are detailed in Appendix B.

Results

Thermal Decomposition

The acrylic paint blast media was essentially converted into a gaseous state, with no residue, during TG analysis. During sample heating, slight mass loss was observed beginning at about 133 °C. Mass loss became rapid at about 250 °C, and began to level off at around 350 °C. Solid acrylic material, which is a light white powder at room temperature, was essentially converted into gasses at temperatures above 420 °C (Figure 1). During TG analysis a weight decrease of 99.75 percent was recorded.

Thermal analysis of urea formaldehyde blast media yielded a more complex mass loss curve, and a residue was left even after heating the media to 1200 °C. The weight change was 87.7 percent (as shown in Figure 2). Observable mass loss began to occur at 65 °C and continued until about 780 °C, with major inflection points at 258 °C, 360 °C, 520 °C, and 678 °C.

The ground walnut shell blast media, which also contained some fruit pits, was also subjected to TG analysis. Sample mass loss began at about 55 °C and ended at about 670 °C. Less than 1 percent of the original mass was left over as residue; the total weight change was 99.02 percent (Figure 3).

Volume of Gases Produced

During LTA experiments to determine the gaseous volume generated by paint blast media samples, significant amounts of smoke were produced. A light-colored smoke was observed during ashing of the acrylic material. Generated smoke from ground walnut shell and urea formaldehyde was denser and darker in color. The ground walnut shell media produced a significant amount of dark liquid condensate. Calculated gaseous combustion exhaust volumes, from integrated mass flow rate data (Table 8) were used to estimate the undiluted significant VOC concentrations in the smoke (Tables 9, 10, and 11). Gaseous volumes data also were plotted versus time (Appendix B). Note that the major portion of combustion effluent is generated during the first minute or two of a timed LTA experiment. With the urea formaldehyde media, off-gassing continued at a slower rate for approximately 20 minutes. Since the ashing

process is exothermic, the experimental setpoint temperature of 575 °C was slightly exceeded during combustion experiments. Actual transient temperatures approaching 620 °C were observed briefly during ashing before dropping back to the setpoint temperature.

Characterization of Significant Volatile Organic Compounds (VOCs) Produced

Clearly, products generated by the combustion of paint blast media represents a very complex mixture. The reconstructed total ion chromatograms from a chamber blank and for the vapor phase samples generated from the combustion of paint blast materials of the ground walnut shell, acrylic, and urea formaldehyde media are presented in Appendix B. Because of the complex nature and overly abundant constituents present in each of the vapor phase samples, the effort was focused on the identification of major components. Those components represent a chromatographic area equal or greater than 1.0 percent of the total chromatographic area.

Electron impact (EI) mass spectral data obtained from thermal desorption (TD) and gas chromatography/mass spectroscopy (GC/MS) analyses were used to carry out identification. Identification of most components was based on the best match of the mass spectral pattern with those provided in the *Eight Peak Index Mass Spectra*, 3d ed. (Royal Society of Chemistry 1983). For components without a match (or with a poor match), chemical structures were postulated to best correlate with the observed fragmentation patterns. Tables 9–11 list compounds that have been tentatively identified in the sample traps. Their estimated quantities ($\mu\text{g/L}$), as determined based on the response factor of d_6 -benzene, were also listed. Chemical nomenclature in the tables refer to general chemical structures, which may include structural isomers with the same chemical formula.

The ground walnut shell media generated predominantly oxygen-containing compounds upon combustion. The abundance of components with furan, phenol, and catechol moieties may be derived from lignin polymer. Because this sample trap was used with a mass range of 35–500 atomic mass units (amu), the water peak was not detected.

The acrylic blast material produced abundant quantities (approximately 5 $\mu\text{g/L}$) of methyl methacrylate (methyl ester of methacrylic acid) from the combustion process. Other compounds containing methacrylic acid moiety were also detected. Significant amounts of water accumulated on the sample trap most likely came from the combustion products or from the ambient air being used to purge the combustion chamber during sampling. Although the sorbent materials in triple absorbent traps (TST) are

hydrophobic, excess amounts of water are retained on the traps despite purging with 1 liter of helium prior to TD step.

The urea formaldehyde blast material is made of polymerized urea formaldehyde (98 percent) with alpha cellulose filler. The hazardous decomposition products or by-products for this material as listed in the Material Safety Data Sheets (MSDS) are smoke, carbon monoxide, carbon dioxide, formaldehyde, and hydrogen cyanide. Significant amounts (0.5 $\mu\text{g/L}$) of carbon dioxide [mass/atomic number (m/z) = 44] have been detected in the air peak along with m/z 28 ions, which is a molecular ion for either carbon monoxide or nitrogen. The selective ion mode was used to obtain mass chromatograms of m/z 27 and 26 (the two most abundant ions for hydrogen cyanide) to search for the presence of hydrogen cyanide. Experimental details are presented in Appendix B. A similar procedure was employed to search for the presence of formaldehyde; none of the early eluting components exhibited the expected characteristic ions generated from formaldehyde. It was determined through consultations that Carbosieve S-II sorbent in the TST is not expected to retain formaldehyde. In addition, Carbosieve S-III is not an ideal sorbent for hydrogen cyanide. Other major components found in the trap include alkyl nitriles, alkylamides of various chain lengths, and compounds with alcohol and furan moieties.

Summary of LTA Results

Temperatures required for media waste volume reduction differ depending on the waste type being processed. Treatment of acrylic media would probably involve effective, almost total reduction of the polymer at temperatures under 400 °C. Processing the ground walnut shell media and especially the urea formaldehyde media would most likely require a cost-benefit analysis to determine the degree of volume reduction desired as compared to the energy expenditure necessary to accomplish it. Temperature inflection points may indicate good management control points in the waste volume reduction process. Mass loss rates, detailed above, may have implications for waste processing time and power consumption during different steps in the LTA process. Weight loss measurements on virgin media indicated that the weight of urea formaldehyde media decreased by 87 percent at 800 °C, and ground walnut shell media decreased in weight by more than 99 percent at 700 °C.

Discussion

LTA is basically low-temperature incineration. Although the experimental design used triple sorbent traps to capture volatile organics, the sorbent was not effective in trapping formaldehyde and hydrogen cyanide. These components may be produced

during LTA and perhaps were present in the combustion effluent of urea formaldehyde media even though the triple sorbent traps used did not effectively capture those compounds. Both formaldehyde and hydrogen cyanide are classified as hazardous air pollutants under the Clean Air Act. The thermal decomposition of the agricultural media generated phenol, and the polymerized urea formaldehyde generated toluene—also classified as hazardous air pollutants. Any volatilized heavy metal contaminants would be classified as hazardous air pollutants. The difficulty of obtaining regulatory approval for any incineration process makes it unlikely that this process could successfully be implemented at Army facilities.

In addition to the air pollution concerns, most of the heavy metal contaminants would be expected to remain in the ash residue, and would require further treatment disposal. Use of LTA at Army maintenance facilities is not recommended at this time.

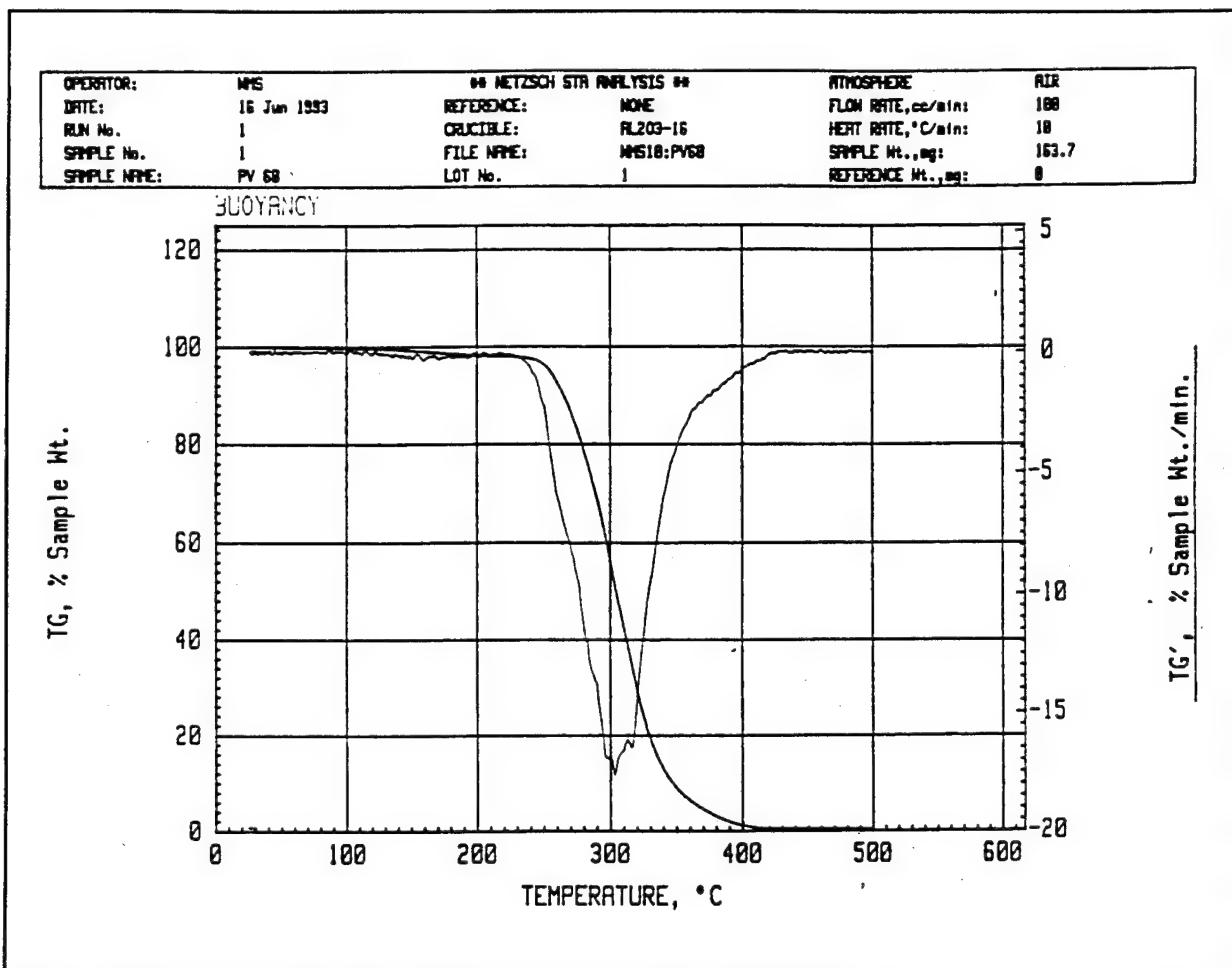


Figure 1. Mass loss for acrylic blast media during LTA for media sample PV60.

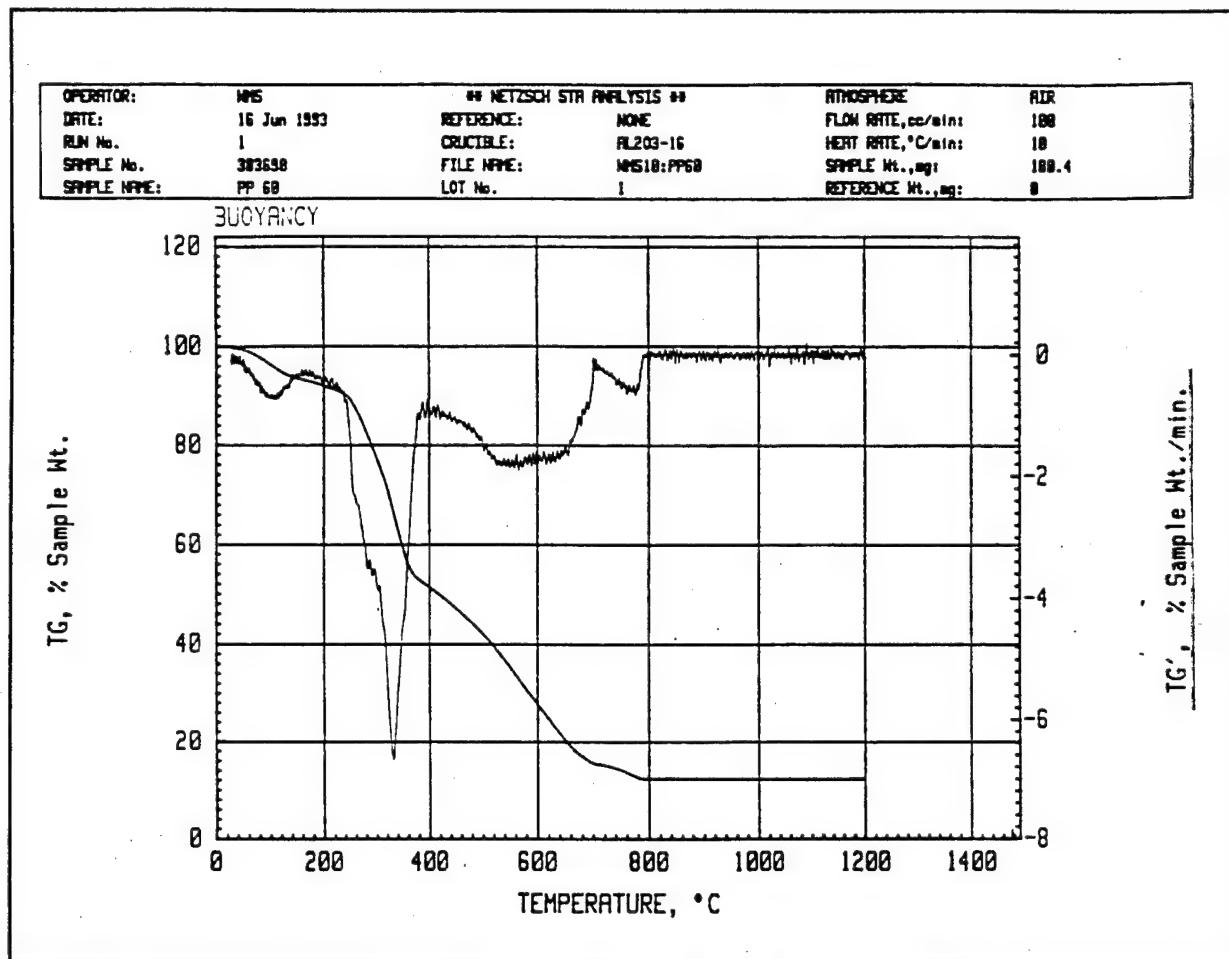


Figure 2. Mass loss for urea formaldehyde blast media during LTA for media sample PP60.

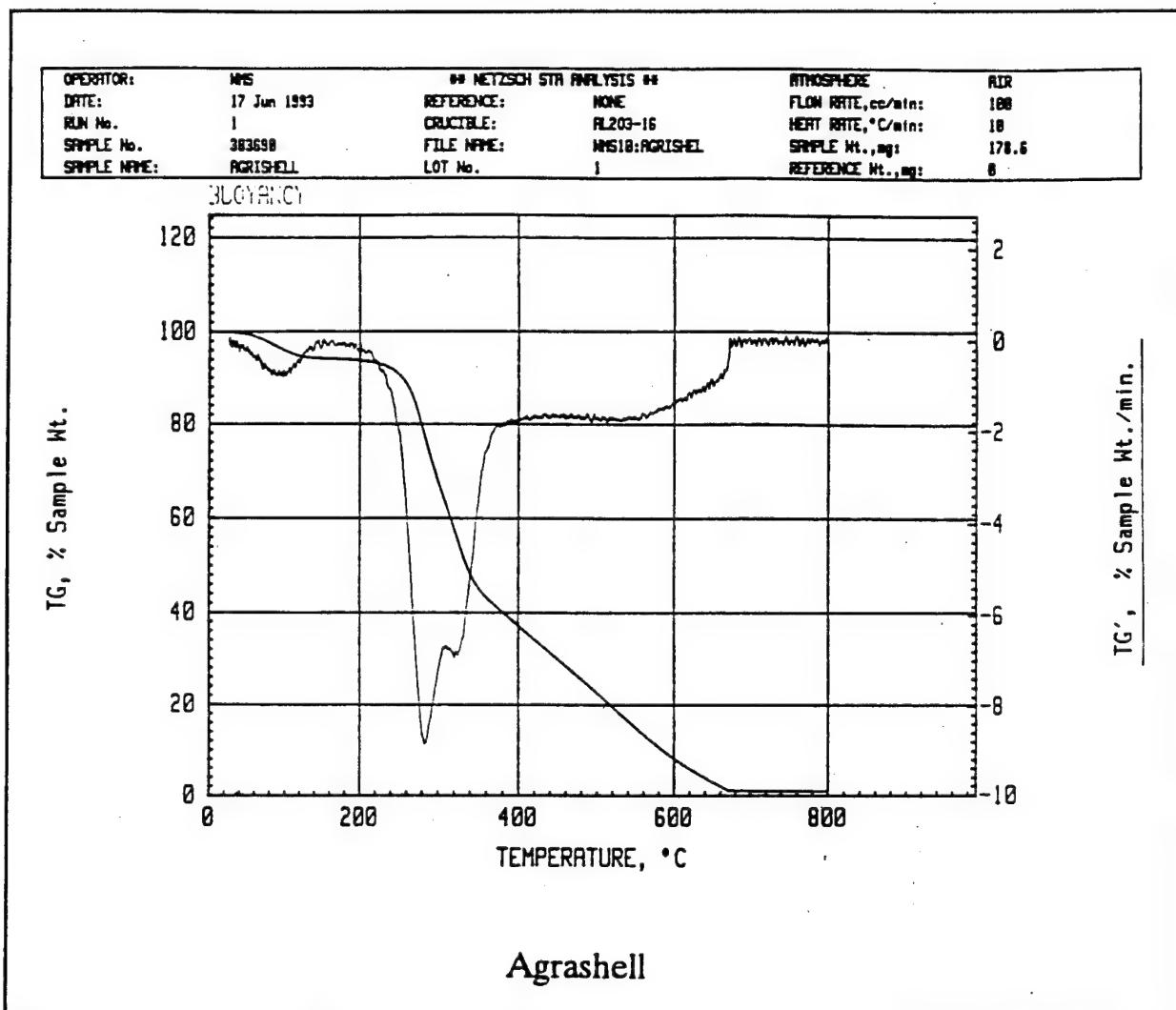


Figure 3. Mass loss for ground walnut shell blast media during LTA.

Table 8. Gaseous exhaust generated during low-temperature ashing.

Paint Blast Media	Ground Walnut Shells	Urea formaldehyde	Acrylic
Sample			
Net Volume	0.873 L	1.899 L	1.212 L
Total Exhaust Volume	10.873 L	11.899 L	11.212 L
Net Mass	0.999 g	0.878 g	1.012 g

*Net gaseous volumes were obtained by subtracting the air affluent volume from the total gaseous volume generated during LTA experiment. Sample residues remaining after ashing were subtracted from the total sample mass to obtain the net mass.

Table 9. Volatile organic compounds collected from low-temperature ashing of ground walnut shell paint blast media.

Compound Tentatively Identified	Retention Time (min.)	Exhaust Conc. (mg/m ³)	Chamber Conc. (mg/m ³)
2-propanol	6.42-8.87	418.5	3.25
methyl acetate	9.28	95.3	0.74
propanoic acid	11.45	57.9	0.45
methyl ester of pyruvic acid	11.93	101.7	0.79
furancarboxaldehyde	12.62	158.4	1.23
butanone	13.57	88.8	0.69
acetyl-oxy-porpanone	13.68	119.8	0.93
methyl-furanone	14.08	63.1	0.49
3,4-dihydro-3H-pyran	15.03	88.8	0.69
methyl-furanone (isomer of 14.08 min peak)	15.32	200.9	1.56
phenol	16.20	90.1	0.70
dihydroxy-cyclobutene-dione	16.88	96.6	0.75
methyl-cyclopentane-dione	17.50	77.3	0.60
methyl-phenol	18.10	61.8	0.48
methoxy-phenol	18.58	202.2	0.57
mixture of oxygenated compounds	19.07	119.8	0.93
dimethoxy benzene	20.42	114.6	0.89
benzene-diol	20.70	76.0	0.59
C ₂ -methoxy-phenol	21.85	124.9	0.97
isomer of C ₂ -methoxy-phenol	22.08	73.4	0.57
C ₂ -phenol	22.47	108.2	0.84
dimethoxy-phenol	23.03	193.1	1.5
hydroxy-methoxy-benzaldehyde	23.98	47.6	0.37
trimethoxy-benzene	24.42	100.4	0.78
methoxy-propenyl-phenol	24.52	68.24	0.53
C ₂ -biphenyl	25.50	52.8	0.41
C ₁ -fluorene	26.17	63.1	0.49
mixture of oxygenated compounds and isomers	26.48-26.75	226.6	1.76
dimethoxy-hydroxy-benzaldehyde	27.93	117.2	0.91
dimethoxy-propenyl-phenol	28.37	85.0	0.66
phenyl-acetophenone	29.23	48.9	0.38
dimethoxy-propenyl-benzene	29.48	54.1	0.42
trihydroxy-methylphenyl-butanone	29.85	67.0	0.52
hexadecanoic acid	35.05	115.9	0.90
hydroxy-dimethoxy-phenyl-propenal	35.52	96.6	0.75

Table 10. Volatile organic compounds collected from low-temperature ashing of acrylic paint blast media.

Compound Tentatively Identified	Retention Time (min.)	Exhaust Conc. (mg/m ³)	Chamber Conc. (mg/m ³)
carbon dioxide	2.53	191.1	1.53
water	3.50-5.58	144.8	1.16
methyl ester of methacrylic acid	9.32-10.44	576.9	4.62
methyl ester of pentenoic acid	12.15	31.2	0.25
hexamethyl-cyclotrisiloxane	12.42	36.2	0.29
C ₂ -alkanol	13.38	121.1	0.397
isomer of 12.15 min peak	13.70	25.0	0.20
alkanol	14.33	201.0	1.61
methyl ester of alcanoic acid	15.35	72.4	0.58
methyl ester of methyl-cyclohexyl carboxylic acid	16.35	38.7	0.31
C ₄ -dioxane	17.77	30.0	0.24
methoxy-pentenyl acetate	18.38	68.7	0.55
C ₄ -cyclopentane-dione	20.53	28.7	0.23
propyl ester of cyclopentenyl acetic acid	21.35	18.7	0.15
propyl ester of methacrylic acid	22.18	38.7	0.31
alkyl-ester of methacrylic acid	22.47	35.0	0.28
C ₆ -cyclopentene	22.60	33.7	0.27
methyl ester of phenoxy-acetic acid	23.12	37.5	0.30
isomer of above	23.42	32.5	0.26
phthalate	72.57	196.0	1.57

Table 11. Volatile organic compounds collected from low-temperature ashing urea formaldehyde paint blast media.

Compound Tentatively Identified	Retention Time (min.)	Exhaust Conc. (mg/m ³)	Chamber Conc. (mg/m ³)
carbon dioxide	2.10	58.8	0.50
water	2.77-4.98	62.4	0.53
mixture of propanol and others	7.83	34.1	0.29
dimethyl-amino-acetonitrile	10.18	27.1	0.23
toluene	10.75	7.1	0.06
N-methyl-formamide	11.87	41.2	0.35
furancaboxaldehyde	12.63	5.9	0.05
1H-imidazole-2-methanol	13.45	30.6	0.26
furanone	14.90	21.2	0.18
oxygenated compounds (possible alkanol)	21.2	27.1	0.23
napthalene	23.67	40.0	0.34
alcanoic acid	26.60	10.6	0.09
n-tetradecanenitrile	31.93	12.9	0.11
methyl ester of alcanoic acid	32.28	9.4	0.08
n-hexadecanenitrile	38.37	24.7	0.21
methyl ester of alcanoic acid	38.77	20.0	0.17
n-alkylamide	41.92	42.4	0.36
n-alkylamide	55.18	36.5	0.31

5 Chemical Separation

Objective of the Technology

Treatment of contaminated abrasive blasting wastes by chemical separation (acid extraction and digestion) was investigated. Conceptually a multistage process was envisioned involving acid extraction of metal contaminants and subsequent alkaline precipitation of metal salts. The decontaminated media would be landfilled while the precipitated metals would require disposal as a hazardous waste. The purpose of this work was to develop an acid digestion process that would be suitable for all types of blast media waste.

Acid Extraction and Digestion Processes

A series of laboratory experiments was performed at USACERL to determine the feasibility of the process. Samples of contaminated blast media waste were collected from Army maintenance facilities and subjected to various digestion processes using citric acid, ethylenediaminetetraacetic acid (EDTA), nitric acid, sulfuric acid, or hydrochloric acid. Leachable metal concentrations of the principal contaminants—Pb, Cd, and Cr—were measured using TCLP before and after acid digestion.

The experimental series was dynamic in that the experimental results from one series of extraction experiments gave insights that led to the design of subsequent experiments. The initial series of extractions used 5 percent, 10 percent, and 20 percent concentrated sulfuric acid for 24 hours. In an attempt to raise the pH value of the waste solution following the extraction, a series of 7 to 12 rinses with water followed an extraction using 5 percent sulfuric acid for 24 hours. A more aggressive rinse using a NaOH/H₂O solution was also evaluated. Other acids, such as citric acid, EDTA, and nitric acid, were evaluated for use as the extraction solution. EDTA in combination with HCl was also tested. These acids were subsequently rejected, and a new series of extraction using 5 percent hydrochloric acid for 24 hours, and 5 percent nitric acid for 24 hours were performed. Subsequent work settled on the use of nitric acid as the extraction solution. The effect of nitric acid concentration was further evaluated.

To monitor the performance of the analytical procedures used, quality-control matrix spikes are called for in the TCLP protocol. The matrix spikes were added at a concentration equivalent to the corresponding regulatory level. The results of these quality-control tests are shown in Appendix C.

Results of Chemical Separation Experiments

The initial series of extractions used 5 percent, 10 percent, and 20 percent concentrated sulfuric acid for 24 hours on coal slag, mixed plastic, and glass bead blast media (Table 12). TCLP results showed a decrease in the leachable cadmium and an increase in the leachable Pb and Cr. Pb and Cr are amphoteric, with increasing solubility at high and low pH. At the low pH of the concentrated sulfuric acid extraction solution, Pb and Cr solubilities are very high.

In an attempt to raise the pH of the waste solution following extraction, an extraction solution using 5 percent H_2SO_4 for 24 hours was followed by a single rinse, either with distilled water or NaOH solution. The water rinses raised the final pH to 4.0 while the NaOH rinse raised the final pH to between 7.3 and 7.7. TCLP results showed that the leachable Cd and Cr decreased, and the Pb increased, compared to the received waste (Table 13). The increase in the TCLP results was higher for samples rinsed with NaOH solution compared to the distilled water.

A 5 percent sulfuric acid extraction for 24 hours, followed by a series of multiple rinses using a NaOH/ H_2O solution, was subsequently evaluated. A water rinse followed by centrifuge and decanting of the rinse solution was repeated between 7 and 13 times, yielding final pH of between 4.3 and 5.0. The TCLP results showed that the leachable Cd and Cr decreased and that the leachable Pb increased (Table 14).

Alternative acids were then considered for use as extraction solutions. A 0.002M* citric acid extraction for 24 hours, followed by three water rinses, was performed on coal slag and glass bead blast media wastes. The rinse solutions were retained and the metal concentration determined (Table 15). The metal content decreased in successive rinse solutions. The TCLP results for the washed and rinsed blast media wastes showed the Cd and Cr to have decreased but there was no change in the TCLP results for Pb.

Other acids, such as EDTA, hydrochloride, and nitric acid, were evaluated for use as extraction solutions. The use of EDTA in combination with hydrochloric acid was also evaluated (Tables 16 and 17). The HCl extraction produced TCLP results showing the

* M: molar concentration.

leachable Cr to increase from the mixed plastic and glass waste, and for the leachable Pb to increase from the coal slag blast media waste.

An acid extraction using 100 ml 0.1M EDTA plus 2 ml HCl for 24 hours caused the Cd and Cr TCLP results to decrease, and the Pb TCLP results to increase. When either 0.1 M EDTA or 5 percent nitric acid were used by themselves as the extraction fluid for 24 hours, the TCLP results for Cd, Cr, and Pb decreased (Tables 16 and 17). However, due to the higher cost of EDTA compared to nitric acid, subsequent work focused on nitric acid as the extraction fluid.

The effect of nitric acid concentration was evaluated. Extractions using 1 percent, 3 percent, and 5 percent solutions on coal slag, mixed glass, and plastic blast media wastes were conducted. The extractions resulted in a decrease in the leachable Cd, Cr, and Pb as determined by using TCLP. No appreciable difference was detected between the 3 percent and 5 percent nitric acid extraction solutions (Table 18).

The effect of acid concentration on the TCLP results for Pb was specifically evaluated using nitric acid extraction solutions in concentrations of 0.5 percent, 1 percent, and 2 percent. The filtrates were retained and the metal contents determined (Table 19). The TCLP results for Pb decreased for all three concentration levels. The Pb content of the retained filtrate was 262 ppm in the 2 percent extraction solution, and 0.97 ppm in the 0.5 percent extraction solution.

To verify the effectiveness of nitric acid extraction on various waste streams, glass beads and plastic blast media wastes were also tested (Tables 20-21). The TCLP results for Cd, Cr, decreased while the TCLP Pb results for the plastic media showed a slight increase. Again, the more concentrated extraction fluids resulted in higher metal contents in the retained filtrates.

Various acid digestion processes using citric acid, EDTA, nitric acid, sulfuric acid, or hydrochloric acid were evaluated. A 16-hour extraction using 2.0 percent nitric acid followed by multiple rinses with deionized (DI) water was determined to be the best extraction process.

Discussion

Acid treatments were found to decrease leachable heavy metal concentrations as measured by TCLP. However, post-treatment total metals concentrations were still quite high. Table 22 shows metal concentrations of the extraction fluid following a

nitric acid extraction and following a different extraction using a LiBO₂ (lithium metaborate) flux at 1000 °C for 5 minutes. The nitric acid extractions were found to remove only 0.1 percent of the total chromium and 0.2 percent of total barium, compared to the LiBO₂ flux. Thus although the leachable component of metal decreased by acid extraction, the largest portion of hazardous metal contaminants was not removed by acid digestion. The acid digestion processes removed only a fraction of the total heavy metal contaminants. Use of these processes is not recommended.

Table 12. TCLP results for sulfuric acid extraction.

Sample	Lab ID	Extraction	Conc.	Time (days)	Cd (ppm)	Cr (ppm)	Pb (ppm)
Coal Slag ANAD	800863	As Received			BDL	0.4	BDL
	800863	H ₂ SO ₄	5%	1	BDL	BDL	12
	800863	H ₂ SO ₄	10%	1	BDL	0.1	15
	800863	H ₂ SO ₄	15%	1	BDL	0.1	20
	800863	H ₂ SO ₄	5%	2	0.1	BDL	7
	800863	H ₂ SO ₄	10%	2	BDL	0.1	7
	800863	H ₂ SO ₄	15%	2	BDL	BDL	8
Mixed Plastic Media SAAD	800864	As Received			5.2	N/A	BDL
	800864	H ₂ SO ₄	5%	1	1.8	51.8	15
	800864	H ₂ SO ₄	10%	1	0.9	35.3	13
	800864	H ₂ SO ₄	15%	1	1.7	58.8	2
	800864	H ₂ SO ₄	5%	2	0.1	0.3	11
	800864	H ₂ SO ₄	10%	2	0.2	0.3	11
	800864	H ₂ SO ₄	15%	2	0.2	0.5	11
Glass Beads - CCAD	800958	As Received			31.6	2.3	0.7
	800958	H ₂ SO ₄	5	1	BDL	BDL	BDL
	800958	H ₂ SO ₄	10%	1	BDL	BDL	BDL
	800958	H ₂ SO ₄	15%	1	BDL	BDL	BDL
	800958	H ₂ SO ₄	5%	2	0.1	BDL	0.7
	800958	H ₂ SO ₄	10%	2	BDL	BDL	BDL
	800958	H ₂ SO ₄	15%	2	BDL	BDL	BDL
Quality Control							
Glass Beads	800958			1	0.02	0.01	0.1
		+ 10 ppm Cd, Cr, Pb		1	9.4	11.5	7.6
		% Recovery			94	115	75
	800958			2	0.04	0	0.24
		+ 10 ppm Cd, Cr, Pb			0.91	0.11	8.42
		% Recovery		2	109	101	82

Table 13. TCLP results for sulfuric acid extraction followed by NaOH rinse.

Sample	ID	Test	Extraction	Conc	Time (hours)	Rinse	pH Final	Cd (ppm)	Cr (ppm)	Pb (ppm)
As Received	800863	Total Metals	(Lab A)					386	259	40.7
As Received	800863	TCLP	(Lab B)					0.628	0.947	4.96
Coal Slag	800863	TCLP	H ₂ SO ₄	5%	24	NaOH	7.7	BDL	BDL	11.0
	800863	TCLP	H ₂ SO ₄	5%	24	NaOH	7.3	BDL	BDL	10.3
As Received	800958	Total Metals	(Lab A)					472	91.4	13.6
As Received	800958	TCLP	(Lab B)					31.6	2.3	0.7
Glass Beads	800958	TCLP	H ₂ SO ₄	5%	24	Water	4.0	BDL	BDL	0.2
	800958	TCLP	H ₂ SO ₄	5%	24	Water	4.0	BDL	BDL	0.3
Blank								BDL	BDL	BDL
Quality Control	800863	TCLP	(Lab B)			NaOH	7.7	0.02	0.1	11.04
	800863									
	+10 ppm Cd, Cr, Pb	TCLP	(Lab B)			NaOH	7.7	10.32	9.8	17.95
% Recovery								103%	97%	69.1%

Table 14. TCLP results for sulfuric acid extraction followed by multiple water rinses.

Sample	ID	Test	Extraction	Conc %	Time hours	Rinse	No of Rinses	pH Final	Cd ppm	Cr ppm	Pb ppm
As Received	800863	Total Metals	(Lab A)					386	259	40.7	0.94
As Received	800863	TCLP	(Lab A)					0.628	7	4.96	
Coal Slag	800863	TCLP	H ₂ SO ₄	5%	24	Water	13	5.0	0.03	0	4.3
	800863	TCLP	H ₂ SO ₄	5%	24	Water	13	4.8	0.05	0	5.3
	800863	TCLP	H ₂ SO ₄	5%	24	Water	7	4.4	0.05	0	6.1
	800863	TCLP	H ₂ SO ₄	5%	24	Water	7	4.3	0.04	0	7.2
Blank								0.04	0	0.8	
Quality Control											
	800863	TCLP	H ₂ SO ₄	5%	24	Water	13	5.0	0.03	0	4.3
	800863 + 10 ppm Cd Cr Pb	TCLP	H ₂ SO ₄	5%	24	Water	13	5.0	11.12	9.7	14.3
% Recovery								111%	97%	100%	

Table 15. Citric acid extraction results.

Sample	ID	Test	Extraction	Conc	Time hours	Rinse	No of Rinses	pH Final	Cd ppm	Cr ppm	Pb ppm
As Received	800863	Total Metals	(Lab A)					386	259	40.7	0.62
As Received	800863	TCLP	(Lab A)					8	0.947	4.96	
Coal Slag	800863	TCLP	Citric Acid	0.02M	24	Water	3		0.1	0.2	4.8
1st Rinse									0.7	4.5	34.9
2nd Rinse									0.2	0.9	8.2
3rd Rinse									0.1	0.3	2.3
As Received	800958	Total Metals						472	91.4	13.6	
As Received	800958	TCLP						31.6	2.3	0.7	
Glass Beads	800958	TCLP	Citric Acid	0.02M	24	Water	3		0.1	0.1	0.4
1st Rinse									24.2	3.6	1.3
2nd Rinse									3.1	0.4	0.4
3rd Rinse									0.3	0.1	0.3
Quality Control									0.1	0.2	4.8
	800863	TCLP									
	800863 + 10 ppm Cd Cr Pb	TCLP							7.7	9.9	15.3
% Recovery									76%	97%	105%

Table 16. Results for EDTA, nitric acid, and hydrochloric acid extraction from waste sample 800863.

Sample	ID	Test	Extraction Fluid	Conc	Time hours	Rinse	No of Rinses	pH Final	Cd ppm	Cr ppm	Pb ppm
As Received	800863	Total Metals	(Lab A)					386	259	40.7	
As Received	800863	TCLP	(Lab B)					0.37	BDL	BDL	
Coal Slag	800863	TCLP	EDTA	0.1M	24	Water	5	0.29	0.3	1	
Filtrate								5.92	17.78	139	
3rd Rinse								0.16	0.07	0.7	
5th Rinse								0.12	0.01	0.2	
As Received	800863	TCLP						0.37	BDL	BDL	
Coal Slag	800863	TCLP	Nitric	5%	24	Water	5	0.05	0.01	0.1	
Filtrate								7.28	87.64	355.2	
3rd Rinse								0.12	0.06	0.5	
5th Rinse								0.1	0.016	0.16	
As Received	800863	TCLP						0.37	BDL	BDL	
Coal Slag	800863	TCLP	EDTA + HCl	0.1M 2%	24	Water	5	0.46	0.04	6.3	
Filtrate								5.32	75.74	205.02	
3rd Rinse								0.16	0.08	0.7	
5th Rinse								0.11	0.02	0.5	
As Received	800863	TCLP						0.37	BDL	BDL	
Coal Slag	800863	TCLP	HCl Acid	5%	24	Water	5	0.19	0.02	1.9	
Filtrate								3.56	41.16	152.48	
3rd Rinse								0.1	1.02	4.9	
5th Rinse								0.07	0.01	0.3	

Table 17. Results for EDTA, nitric acid, and hydrochloric acid extraction of waste sample 800963.

Sample	ID	Test	Extraction Fluid	Conc %	Time hours	No of Rinse	pH Final	Cd ppm	Cr ppm	Pb ppm
As Received	800963	Total Metal	(Lab A)					16.7	256	888
As Received	800963	TCLP	(Lab A)					0.783	0.65	4.41
Plastic/Glass	800963	TCLP	Water		24	Water	5	25.25	2.36	1.2
Filtrate								25.69	107.84	0.48
3rd Rinse								2.17	8.83	0.1
5th Rinse								0.9	2.16	0.1
As Received	800963	TCLP						0.783	0.65	4.41
Plastic/Glass	800963	TCLP	EDTA	0.1M	24	Water	5	0.64	1.89	0.4
Filtrate								268.21	127.12	17.31
3rd Rinse								8.08	4.2	0.7
5th Rinse								0.96	1.2	0.7
As Received	800963	TCLP						0.783	0.65	4.41
Plastic/Glass	800963	TCLP	Nitric Acid	5%	24	Water	5	1.05	0.1	0.1
Filtrate								252.17	251.35	251.35
3rd Rinse								3.68	1.29	1.29
5th Rinse								0.85	0	0.04
As Received	800963	TCLP						0.783	0.65	4.41
Plastic/Glass	800963	TCLP	HCl Acid	5%	24	Water	5	2.1	0.13	0.13
Filtrate								199.76	167.85	167.85
3rd Rinse								8.28	1.28	1.28
5th Rinse								3.25	0.04	0.04

Table 18. Nitric acid extractions from waste sample 800863.

Sample	ID	Test	Extraction Fluid	Conc %	Time hours	No of Rinse	pH Final	Cd ppm	Cr ppm	Pb ppm
As Received	800863	Total Metal						386	259	40.7
As Received	800863	TCLP						0.628	0.947	4.96
Coal Slag	800863	TCLP	Nitric Acid	1%	24			0	0.20	0.30
	800863	TCLP	Nitric Acid	3%	24			0	0	0.03
	800863	TCLP	Nitric Acid	5%	24			0.01	0	0.03
	800863	TCLP	HCl Acid	5%	24			0	0	0.72
As Received	800963	Total Metals						16.7	256	888
As Received	800963	TCLP						0.783	0.65	4.41
Plastic/Glass	800963	TCLP	Nitric Acid	1%	24			0.01	0.50	0.06
	800963	TCLP	Nitric Acid	3%	24			0.01	0.21	0.10
	800963	TCLP	Nitric Acid	5%	24			0.02	0.14	0.16
	800963	TCLP	HCl Acid	5%	24			0.09	0.11	0.10

Table 19. Nitric acid extraction results for lead.

Sample	ID	Test	Extraction Fluid	Conc %	Time hours	Rinse	No of Rinses	pH Final	Pb ppm	Pb ppm	Average Pb ppm
As Received	800863	Total Metal	(Lab B)					727.8		727.8	
As Received	800863	TCLP	(Lab B)					3.29	3.29	3.29	
Coal Slag	800863	TCLP	DI Water		16	Water	3	3.38	3.38	3.29	
Filtrate								0	0	0	
Rinse 1								0	-0.02	-0.01	
Rinse 2								0	0	0.01	
Rinse 3									-0.01	-0.01	
As Received	800863	TCLP						3.29	3.29	3.29	
Coal Slag	800863	TCLP	Nitric Acid	0.5%	16	Water	3	1.70	1.57	1.64	
Filtrate								0.96	0.98	0.97	
Rinse 1								0.33	0.35	0.34	
Rinse 2								0.22	0.25	0.24	
Rinse 3								0.22	0.24	0.23	
As Received	800863	TCLP						3.29	3.29	3.29	
Coal Slag	800863	TCLP	Nitric Acid	1.0%	16	Water	3	1.44	1.42	1.43	
Filtrate								86.40	N/A	86.40	
Rinse 1								8.73	8.82	8.78	
Rinse 2								3.81	3.88	3.85	
Rinse 3								2.35	2.33	2.34	
As Received	800863	TCLP						3.29	3.29	3.29	
Coal Slag	800863	TCLP	Nitric Acid	2.0%	16	Water	3	1.52	1.38	1.45	
Filtrate								262.50	N/A	262.50	
Rinse 1								16.93	17.07	17.00	
Rinse 2								8.98	9.11	9.05	
Rinse 3								4.38	4.43	4.41	

Table 20. Nitric acid extraction results for glass media waste sample 800961.

Sample	ID	Test	Extraction Fluid	Conc %	Time hours	Rinse	No of Rinses	pH Final	Cd ppm	Cr ppm	Pb ppm
As Received	800961	Total Metal (Lab A)						20.7	20.7	142.1	
As Received	800961	TCLP (Lab B)						0.72	BDL	5.05	
Glass Beads	800961	TCLP	DI		16	Water	3	0.05	0.96	0.26	
Filtrate								0.11	0.32	0.01	
Rinse 1								0.08	0.01	0	
Rinse 2								0.08	0	0	
Rinse 3								0.05	0	0	
As Received	800961	TCLP									
Glass Beads	800961	TCLP	Nitric Acid	0.5%	16	Water	3	0	0.01	0.01	
Filtrate								13.58	0.61	77.38	
Rinse 1								1.5	0.21	8.12	
Rinse 2								0.15	0.14	0.89	
Rinse 3								0	0.06	0	
As Received	800961	TCLP									
Glass Beads	800961	TCLP	Nitric Acid	2.0%	16	Water	3	0	0	0.01	
Filtrate								13.50	0.92	69.34	
Rinse 1								1.56	0.23	7.65	
Rinse 2								0.18	0.06	0.91	
Rinse 3								0	0.05	0	
As Received	800961	TCLP									
Glass Beads	800961	TCLP	Nitric Acid	5.0	16	Water	3	0	0.03	0.01	
Filtrate								15.74	1.07	71.70	
Rinse 1								1.75	0.25	7.82	
Rinse 2								0.21	0.09	1.00	
Rinse 3								0.02	0.08	0.01	

Table 21. Nitric acid extraction results for PMB waste.

Sample	ID	Test	Extraction Fluid	Conc %	Time Hours	No of Rinse	pH Final	Cd ppm	Cr ppm	Pb ppm
		Total Metal	(Lab B)					39.4	704	675.2
As Received	800968	TCLP	(Lab B)				1.5	11.0	BDL	
Plastic Beads	800968	TCLP	DI		16	Water	3	1.32	4.59	0.44
		Filtrate						0.64	65.64	0.05
		Rinse 1						0.20	21.17	0.04
		Rinse 2						0.13	13.29	0.03
		Rinse 3						0.10	9.40	0
As Received	800968	TCLP								
Plastic Beads	800968	TCLP	Nitric Acid	0.5%	16	Water	3	0.01	0.23	1.19
		Filtrate						22.56	141.75	13.5
		Rinse 1						5.25	35.28	3.32
		Rinse 2						1.2	8.22	1.23
		Rinse 3						0.34	2.66	0.67
As Received	800968	TCLP								
Plastic Beads	800968	TCLP	Nitric Acid	2.0%	16	Water	3	0.00	0.16	0.18
		Filtrate						23.06	425.75	164.00
		Rinse 1						5.43	31.00	48.29
		Rinse 2						1.31	23.41	12.50
		Rinse 3						0.37	7.23	3.95
As Received	800968	TCLP								
Plastic Beads	800968	TCLP	Nitric Acid	5.0	16	Water	3	0.00	0.20	0.70
		Filtrate						20.86	482.50	220.00
		Rinse 1						4.70	94.00	51.81
		Rinse 2						1.09	23.85	3.60
		Rinse 3						0.28	8.62	5.15

Table 22. Comparison of nitric acid and LiBO₂ flux digestion for metals analysis.

Test No.	Sample	Test	Cd ppm	Pb ppm	Cr ppm	Ba ppm
124	P1	HNO ₃	1.79	34.01	22.99	30.22
125	P1	HNO ₃	1.65	33.08	22.58	30.51
159	P1	LiBO ₂			20557	3044
160	P1	LiBO ₂			17199	2580
133	P2	HNO ₃	1.57	30.14	20.88	28.02
134	P2	HNO ₃	1.46	28.04	19.95	27.16
161	P2	LiBO ₂			18470	2780
162	P2	LiBO ₂			18955	2672
128	P3	HNO ₃	0.41	5.53	6.92	4.36
129	P3	HNO ₃	0.38	5.86	6.91	4.54
163	P3	LiBO ₂			9219	478
164	P3	LiBO ₂			9165	455
135	P4	HNO ₃	0.35	5.39	5.47	4.98
136	P4	HNO ₃	0.39	5.55	5.76	5.13
157	P4	HNO ₃ - LiBO ₂			6842	518
158	P4	HNO ₃ - LiBO ₂			6865	508
138	Glass 5	HNO ₃	4.69	1.38	0.10	0.03
139	Glass 5	HNO ₃	4.44	1.20	0.10	0.03
150	Glass 5	LiBO ₂			4	9
151	Glass 5	LiBO ₂			13	11
142	Glass 6	HNO ₃	0.52	0.39	0.21	0.14
143	Glass 6	HNO ₃	0.39	0.26	0.13	0.09
155	Glass 6	LiBO ₂			45	25
156	Glass 6	LiBO ₂			35	12
145	Sand 7	HNO ₃	0.15	0.75	0.60	1.22
146	Sand 7	HNO ₃	0.15	0.79	0.58	1.15
152	Sand 7	LiBO ₂			810	887
153	Sand 7	LiBO ₂			819	899
165	Sand 7	HNO ₃	14.5	85	70	121
166	Sand 7	HNO ₃	15.5	69	60.35	126
167	Sand 7	LiBO ₂ (after 165#)			689.5	818
168	Sand 7	LiBO ₂ (after 165#)			726.5	804
114	Sand 8	HNO ₃	0.93	0.21	0.19	0.27
115	Sand 8	HNO ₃	0.94	0.15	0.19	0.21
30	Sand 8	LiBO ₂	86		40	704
31	Sand 8	LiBO ₂	82		38	765

6 Biodegradation Through Microbial Digestion

Objective

The term *biodegradation* is often used to describe a variety of quite different microbial processes that occur in natural ecosystems. Biodegradation can be defined as the breakdown of organic compounds in nature by actions of microorganism, such as bacteria, actinomycetes, and fungi. The microorganisms derive energy and may increase in biomass from the process (Riser-Roberts 1992). The breakdown can proceed via either an aerobic or anaerobic digestion process. The difference is that aerobic digestion requires the presence of oxygen, while anaerobic digestion proceeds without oxygen.

The objective was to evaluate the potential of a biodegradation process to either render the contaminated paint blast media waste nonhazardous or to decrease the disposal volume. Bioremediation treatment processes that consist of the biodegradation of organic-based plastic media waste or agricultural-based blast media waste were considered in this study. Bioremediation processes would not be suitable for inorganic blast media such as mineral, slag, or glass abrasives.

Approach

DOT Technologies of Vancouver, BC, has developed a bioremediation process for the successful treatment of solvent-based paint strippers. The process was modified to treat starch-based ground walnut shell blast media wastes generated by the commercial airline industry (Oestreich and Waugh 1993; Oestreich and Waugh 1994). A preliminary evaluation of this process was conducted by USACERL.

The DOT bioremediation process starts with a starch enzyme liquefaction step. To make the starch blast media soluble in water, the starch waste must be dispersed in water and treated with an enzyme. The alpha amylase enzyme is widely used in the starch industry to liquefy starch for the production of syrups and sweeteners. The enzyme particle is specifically designed to cleave the starch polymers, reducing the carbohydrate polymers to simple sugars and low-molecular-weight oligosaccharides.

Following liquefaction, the mixture is filtered through 25- and 15-micron filters. The paint solids that accumulate in the particulate filters, can be directly disposed of as a hazardous waste or further digested. The volume of paint solids collected was typically 5 to 10 percent of the original starch waste volume. The filtered starch solution is then passed through an ion-exchange system to remove metal contaminants, including heavy metals.

The resulting starch solution is transferred to starch waste digestion. A bacteria and nutrient package is added to start the digestion and the starch is degraded over a 5-7 day period. Specific-gravity readings can be used to monitor the solids reduction with time to indicate when the starch has been fully digested. The remaining water is pumped back to disperse the next batch of starch waste, and the process is repeated.

Discussion

The disposal costs for the bioremediation of starch waste were projected by DOT Technologies to compare favorably to current methods of disposal in a hazardous waste landfill. Total cost per pound* were estimated to range from US \$0.50/lb for waste volumes greater than 150,000 lb, to \$0.75 US/lb for waste volumes of less than 50,000 lb.

The advantage of the bioremediation process developed by DOT Technologies is that the process decreases the disposal volume of the hazardous waste.

Disadvantages include the following:

- The complexity of the bioremediation process impacts its feasibility for use on an industrial scale at an Army facility
- Bioremediation requires specialized knowledge and equipment not currently available at most army depot facilities
- The DOT Technologies process was developed specifically for ground walnut shell media; the process can not be modified for use with other media types
- The selection of the bacteria may be specific to the waste stream, requiring different mixtures of bacteria for different waste streams
- The final extraction of the hazardous species in the treatment process and their disposal is ambiguous and needs further clarification

* 1 lb. = 0.4536 kg.

- Abrasive blasting with starch media is not a major depaint method at Army depots.

Considering these disadvantages, the use of a bioremediation process for treating paint blast media waste at Army facilities is not recommended.

7 Self-Encapsulation of Plastic Media Waste

The self-encapsulation of thermoplastic blast media waste was investigated previously by Jermyn and Wichner (1991). The concept consists of heating the thermoplastic Type V - acrylic media, such that it softens to a point that it can be molded into a non-leachable waste form. The self-encapsulation of Type V acrylic waste by softening and pressure molding was shown to pass EPA leachability requirements (Table 23). Thermoset media Types I, II, III, and IV do not melt on heating, but directly decompose. To encapsulate these waste types, they were mixed with a thermoplastic material. The thermoplastic would soften, encapsulating the contaminated thermoset blast media wastes. Table 23 shows that encapsulation with a 1:3 blend of Type II media wastes in Type V thermoplastic material failed the TCLP leachability test for Cd and Cr.

Self-encapsulation of plastic media was found to be effective only with Type V thermoplastic blast media waste. The limited data showed that self-encapsulation was not effective on thermoset media blended into thermoplastic media. Because most depot depaint operations use a variety of both thermoplastic and thermoset plastic media, a treatment process applicable only to one type of plastic medium is of limited utility to the Army.

Table 23. TCLP results for self-encapsulated plastic media waste materials.

	Ba ppm	Cd ppm	Cr ppm	Pb ppm	Status
Type V Waste	1.5	0.83	19	0.07	Passed
Self-encapsulated Type V Pellet	1.0	0.26	2.7	0.82	Passed
Type II Waste	1.5	2.0	29	0.08	Failed Cd, Cr
1:3 Blend, Type II: Type V	1.5	1.2	22	0.07	Failed Cd, Cr
Palletized blend	0.91	1.4	4.5	2.3	Failed Cd
TCLP Limit	100	1	5	5	

Source: Jermyn and Wichner 1991.

8 Waste Stabilization in Portland Cement

Background

Cement-based materials were the first ingredients used in chemical fixation and stabilization of hazardous wastes and have been the most widely used (Connors 1990). Cement stabilization was first used in the processing of nuclear wastes in the 1950s. Cement and cement-based materials for the treatment of both hazardous and radioactive wastes have since been widely studied (Topp 1982; Barth 1990; Canadian Portland Cement Association 1992).

Cement stabilization was investigated as a universal treatment for the waste generated by the full range of media types used at Army depot facilities.

Portland cement was patented in 1824 by Joseph Aspidin and is made by heating together limestone and clay at about 1500 °C. It was named after the natural stone that it resembled from the quarries of Portland, England. Portland cement is a mixture of various calcium silicates and calcium aluminate minerals, principally dicalcium silicate and tricalcium silicate with smaller amounts of tricalcium aluminate and calcium aluminoferrite. These are represented in the cement notation as C_2S , C_3S , C_3A , and C_4AF , respectively. A typical weight proportion of Portland cement is 55 percent C_3S , 25 percent C_2S , 10 percent C_3A , and 10 percent C_4AF .

The cement's reaction process begins with the introduction of water. The water reacts with the silicate mixture of the cement to ultimately form a hard, dense matrix. Although the specific reactions are complex (Lea 1970), it may be considered as a series of reactions between the solid cement components and a fluid (Barneyback and Diamond 1981). The fluid initially is the mixture water, and the solid component is the cement. Shortly after mixing, the water is converted into a complex alkali- and sulfate-bearing solution. On setting, some fluid is captured in the pores of the matrix. Further hydration takes place as the cement components continue to react with the pore solution. The hazardous waste can be either mixed with the dry cement or added to the mixture shortly after the water is mixed in.

The use of a cement system containing superplastizers, fly ash, and silica fume was reported to stabilize paint blast waste (Garner, Carrasquillo, and Fowler 1993).

However, the specific chemical processes that occurred during the solidification were not discussed.

Approach

A multiphase approach was used. In Phase I, blast media waste samples were collected from Army depot facilities. These samples were tested for leachable metals, and those determined to be hazardous were solidified in commercial Portland cement. Cement stabilization was found to yield the paint blast samples nonhazardous for Cd, but the process was not able to stabilize Cr.

In Phase II, additional blast media waste samples were collected and characterized. To simulate the high pH chemical environment encountered during the hydration reaction in a cement matrix, the response of the paint blast media waste to simulated pore solutions was investigated.

In Phase III, the paint blast media wastes were encapsulated in Portland cement. The pore solution, which is the actual chemical environment that the wastes encounter during cement hydration, was expressed from cast cement and waste samples. The metal content of expressed pore solution was analyzed.

In the expectation that granulated blast furnace slag would chemically reduce the valence of the chromium from the waste during the cement hydration reaction, samples of paint blast media wastes were cast in a mixture of Portland cement and blast furnace slag during Phase IV. The complete laboratory results of the cement stabilization work are presented in Appendix C.

Phase I—Cement Stabilization

Paint blast media waste samples were obtained from Army Depot facilities. The concentration of leachable RCRA metals of the as-received wastes was determined by TCLP (Table 24). Five of the 10 wastes were found to be not hazardous and no additional testing was necessary. Cement stabilization of the five samples that failed TCLP was studied. These samples failed TCLP for Cd and/or Cr.

Water is necessary to initiate the cement hydration reaction. However, to form a workable body with adequate flow characteristics, additional water above the stoichiometric requirement is generally added. This is typically described in terms of the water-to-cement ratio, the stoichiometric value being 0.44. Typical commercial

concrete uses a water-to-cement ratio of +/- 0.5. In the Phase I study, 22 percent Portland cement, and 11 percent water by weight were added to the waste. The three waste samples that initially failed TCLP only for Cd were successfully stabilized by this procedure. The remaining two wastes, which initially failed both for Cd and Cr as received, passed TCLP for Cd but failed the TCLP test for Cr after encapsulation. These results indicate that Cd-contaminated waste can be successfully stabilized in Portland cement.

The two wastes that failed the TCLP for Cr in the first stabilization—sand and plastic media from SSAD—were subjected to further evaluation. The wastes were treated by 20 percent Portland cement and 20 percent water additions. These wastes failed the TCLP test for Cr, and subsequently were treated with 33 percent addition of Portland cement and 17 percent water addition. Again the two wastes failed TCLP. These results indicated the difficulty of cement stabilization of Cr-contaminated waste in Portland cement.

Work beyond encapsulation and TCLP testing was necessary to gain insight into the chemical processes occurring during cement solidification. The use of simulated and expressed pore solutions was investigated and is discussed in the sections below.

Phase II—Simulated Pore Solution Analysis

Waste Characterization

Additional paint blast media waste samples generated at an Army maintenance facility were obtained for use in this and subsequent phases of the investigation. The wastes selected were among those more commonly generated at the facility. Samples were taken from a number of blasting stations for each type of media. The total metal (As, Ag, Cd, Hg, Pb, and Se) concentrations were determined by dissolving the sample in a concentrated solution of nitric acid (1 HNO₃ : 1 H₂O) at 80 °C for 12 hours. The Cr and Ba content was determined using a LiBO₂ flux at 1000 °C for 5 minutes. The results are presented in Table 25.

The leachable component of the waste as measured by TCLP using the EPA protocol is shown in Table 26. The results of TCLP analyses showed that seven of the eight wastes failed for Cd, and all plastic media wastes failed for Cr. Despite significant Pb and Ba contents in the raw waste, all wastes passed TCLP for those elements.

Approach

The TCLP is designed to simulate the leaching of a waste form in a municipal landfill along with other general refuse. However, the actual chemical environment that a hazardous species may encounter may be substantially different. Bishop (1988) reported that for cement-based systems, the high alkalinity quickly neutralizes all of the acid present in the leachant, so that the leaching occurs under highly alkaline conditions rather than acidic conditions. Therefore, for waste treated with Portland cement, the measured concentration of metals in TCLP leachate may not accurately represent the true stability of the waste species.

The extraction and analysis of the pore solution from Portland cement has provided insight into the hydration process (Longuet, Burglen, and Zelwer 1973; Barneyback and Diamond 1981). Pore solutions recovered after set are typically found to be concentrated solutions of alkali hydroxides with modest contents of other compounds. The overall pH of the pore solution is extremely alkaline, with a pH >13; this is the chemical environment that any foreign species, introduced from the hazardous waste, would encounter during stabilization. Understanding the behavior of foreign species in this specific chemical environment should give insight into the chemical processes that occur during stabilization. Such an understanding was expected to permit the subsequent optimization of the stabilization matrix to enhance the long-term stabilization of hazardous wastes.

Due to the difficulty of extracting or expressing pore solution from cement samples, and the resulting complex chemistry of the pore solution environment, simulated pore solutions had to be used to model the response of a waste to this environment. An advantage of using simulated pore solutions is that the role of pH on the solubility of metal species in the waste is isolated.

The simulated pore solution used in this study consisted of 1.0M and 0.1M solutions of KOH + NaOH (3:1 mole ratio) corresponding to typical high- and low-alkali Portland cements. Samples of abrasive blast media waste (100g) were placed into 2 liters of model pore solution. After storage in a nitrogen environment for 1 day and 28 days respectively (these are standard mileposts for cement hydration), the samples were filtered and the metal contents determined. Concentrations of As, Ag, Ba, Cd, Cr, Pb, and Se were determined using inductively coupled plasma. The method detection limits (mg/l) are as follows: As = 0.11, Ba = 0.030, Cd = 0.017, Cr = 0.007, Pb = 0.066, Se = 0.18, and Ag = 0.016. A graphite furnace atomic absorption spectrometric method was used to determine Hg content (Keller, Peden, and Rattonetti 1984).

Results

The results of simulated pore solutions for each waste are presented in Table 27. The controlling factor in the response of a waste species to the simulated pore solution is the pH. Due to the high pH of cements, the pH is not directly measured. Instead, the buffering capacity to an acid titration is determined. The predominant anion is assumed to be OH⁻ such that the approximate pH can be calculated. The type of blast media did not seem to have significant effect on the behavior of the metal species in the waste. The length of residence in the simulated pore solution did not greatly affect the concentration of metals in solution.

All blast media wastes failed the TCLP for Cd, but when samples of the waste were exposed to the simulated pore solutions, the concentration of Cd decreased to below 1 ppm. This is consistent with the work of other investigators as summarized by Connor (1990), who reported that Cd was found to be insoluble at the high pH encountered in the model pore solution. Cd begins to leach significantly only below pH 9.

Cr exhibits amphoteric (both acid and basic) behavior with high solubility at both low and high pH (Pourbaix 1974). The plastic blast media wastes failed TCLP due to significant Cr content. When subjected to the chemical environment of the simulated pore solution, the concentration of Cr increased due to the high pH of the solution, and was dependent on the pH (Figure 4). The chromium ion is expected to be present as Cr⁶⁺, which is highly soluble (Pourbaix 1974).

Similar behavior was encountered for Pb-containing wastes. Even though the samples successfully passed TCLP, when subjected to the model pore solutions the concentration of Pb increased with increasing solution pH (Figure 5). This was due to the amphoteric behavior of the Pb. For the highly alkaline conditions of the pore solution, the increased solubility of both Pb and Cr confirmed the controlling role that pH plays in the response of waste species in cement-based matrix. This demonstrates the care which must be taken in interpreting TCLP results for hazardous waste treated in cement.

Next the paint blast media wastes were encapsulated in Portland cement. The actual pore solution was extracted from cast samples of cement and blast media waste to determine directly the chemical response of the hazardous components of the waste to the actual cement hydration environment.

Phase III—Portland Cement Stabilization

Approach

In this phase, the paint blast media wastes analyzed in Phase II were encapsulated in Portland cement. An important goal in stabilization and solidification of any hazardous waste is the final disposal volume generated. In order to minimize the final disposal volume, a loading of 75 percent waste and 25 percent cement (by volume) was utilized. High waste loading also minimizes the raw material costs of the Portland cement used for stabilization.

The exact chemical and mineral makeup of Portland cement depends on the original raw materials utilized. These raw materials tend to vary depending on the local geology of origin, particularly in terms of alkali content. Therefore, in this phase, two commercially available Portland cements were used—one corresponding to the lower limit of alkali content in commercial cements and the other corresponding to the upper limit. Chemical analysis of the high- and low-alkali cements were performed using x-ray fluorescence, and are shown in Table 28.

Paint blast media waste, cement, and water were blended in a planetary mixer, cast with vibration into plastic cylinders approximately 47 x 70 mm, and sealed. Water is necessary to initiate the cement hydration reaction. However, to form a workable body with adequate flow characteristics, additional water above the stoichiometric value is generally added. In this study, water judged to yield suitable workability was added and varied depending on the fineness of the waste media. The water-to-cement ratios are presented in Tables 29 and 30. Samples were allowed to hydrate for 1 day and 28 days (for high- and low-alkali cements, respectively) before pore solutions were expressed.

A schematic of the pore expression apparatus is shown in Figure 6. Compressive loads as high as 500 MegaPascals (MPa) were applied to effectively express pore solutions from the solidified waste specimens. The expressed pore solution was collected and stored under nitrogen atmosphere until analyzed.

Results

The chemical analysis of expressed pore solutions from spent paint blast media wastes incorporated into ordinary Portland cement matrix are given in Tables 29 and 30. The OH-concentration of the pore solution expressed from cement waste forms are lower than those used in the simulated pore solution study—particularly for the plastic media P1 and P2. The high water-to-solid ratio of the waste forms, required due to the

extreme fineness of the spent plastic media, diluted the alkali levels of the pore solutions. Still, the solubility of the hazardous elements in the expressed pore solutions followed the general trends seen in Phase II. The expressed pore solution contained very low concentrations of Cd and Ba (as BaSO₄) in solution because Cd and Ba are insoluble at high pH.

Both Cr and Pb showed significant solubility within the matrix of the solidified waste form. The initial concentration of Cr in the expressed pore solution was much higher after 1 day hydration in both low- and high-alkali cement systems than was seen in the simulated pore solutions. In the expressed pore solutions, Cr increased in concentration with an increase in OH⁻ concentration (Figure 7). However, as shown in Figure 8, samples hydrated 28 days had higher [OH⁻] and lower Cr concentrations compared to samples hydrated 1 day. For longer times, the [OH⁻] concentration increased with hydration time and the Cr concentration decreased. This is opposite to the response expected with [OH⁻] control of the chromium concentration. It seems obvious that additional processes must be occurring. Processes to decrease the chromium concentration in the pore solution may include a very extended reduction process of the chromium or some combination of physical adsorption and/or incorporation of the Cr into the cement hydration products. It appears that the kinetics are sufficiently slow that the process may extend beyond the 28-day hydration period studied.

The concentration of Pb was not controlled by the [OH⁻] of the expressed pore solution (Figure 9). The Pb concentration of samples P1 and P2 decreased despite an increase in the [OH⁻] of the expressed pore solution. Clearly other factors besides the [OH⁻] influenced the solubility of Pb within the actual matrix of ordinary Portland cement waste forms. The lower Pb concentration in the expressed pore solution of the high-alkali cement may possibly be due to the higher sulfate content of the high-alkali cement (Table 28). During normal cement hydration sulfate ions are released into the pore solution. The presence of sulfates would be expected to react with the Pb species present and precipitate out a low-solubility Pb sulfide, resulting in a decrease of the Pb concentration in the pore solution.

TCLP calls for any initial liquid phase present in the waste to be added to the liquid extract, and for these to be analyzed together. The results of the TCLP analysis performed on the solid residue retained after expression of the pore solution are given in Table 31. Due to the trapping of pore solution in the many isolated submicron pores, the expression of pore solution typically only extracts 10 to 25 percent of the total pore solution. The results of TCLP performed on similar samples that did not have the pore solution expressed are shown in Table 32. No significant difference was found in the two sets of TCLP results. The Cr concentration was slightly higher in the

low-alkali cement waste forms compared to the high-alkali cement wastes. TCLP analysis showed no apparent trend due to hydration time.

The plastic media waste samples P1 and P2 stabilized in Portland cement failed TCLP for Cr. The high pH of the cement completely neutralized the acid present in the TCLP test. Both the initial pH and final $[\text{OH}^-]$ of the TCLP test were measured. For samples P1 and P2, the calculated final pH was >12.2 , at which Cr is highly soluble. The Cr metal concentration of samples G5, G6, S7, and S8, which were at least one order of magnitude lower than P1 and P2 (Table 25) all passed TCLP when stabilized in Portland cement.

The final $[\text{OH}^-]$ of the TCLP extraction fluid was in the identical range as the $[\text{OH}^-]$ of the expressed pore solution. The similarity of the $[\text{OH}^-]$ is demonstrated clearly in Figure 10, where the chromium concentration of the expressed pore solutions is plotted on the same graph as the Cr concentration obtained from the TCLP analyses. Both the expressed pore solution and TCLP are at the same high $[\text{OH}^-]$ such that both show the similar high Cr solubility. It is this final pH of the TCLP extraction test, controlled by the alkalinity of the cement, that determines the leachable chromium.

Summary of Phase III Results

Paint blast media wastes were encapsulated in Portland cement. The expressed pore solutions had calculated pH greater than 12. At this pH, Cd and Ba concentrations were low and Cr and Pb concentrations were high. The response of the Cr and Pb concentrations to pH and hydration time were observed. The high pH of the cement completely neutralized the acid present in the TCLP test. Samples P1 and P2, stabilized in Portland cement, failed TCLP for Cr.

Phase IV—Stabilization in Cement and Blast Furnace Slag Addition

Approach

An approach developed by Pourbaix (1974), which is widely used by electrochemists and corrosion engineers, is to represent the stability fields of ionic species on a two-dimensional plot of the electrochemical potential versus pH. The potential-pH diagram for system chromium in water is shown in Figure 11. The stabilization and solidification of Cr^{6+} is typically a two-step process, with an initial reduction of Cr^{6+} to Cr^{3+} by the addition of ferrous salts followed by encapsulation in cement or another type of matrix.

The stability fields for Portland cement and Portland cement with blast furnace slag were superimposed by Macphee and Glasser (1993) onto Figure 11. They showed ordinary Portland cements to have a pH > 13. The addition of blast furnace slag reduced the pH to between 11 and 13, and also reduced the electrochemical potential from oxidizing to reducing. It was inferred that this may be sufficient to reduce the Cr^{6+} in equilibrium with a Portland cement system to Cr^{3+} in a blast furnace slag/cement system. Therefore, to control the stability of the chromium in a solidification matrix, it is necessary to control the electrochemical potential and pH that determines the ionic species and its solubility.

Blast furnace slag is formed during the manufacturing of iron when limestone reacts with the silica and alumina present in the ore as impurities. Blast furnace slag is a pozzolanic material; although it will not hydrate directly with water, when combined with cement it will participate in the cement hydration reaction. The addition of blast furnace slag to Portland cement is known to slow the hydration kinetics and to increase the final compressive strength of the cement (Taylor 1990).

The addition of blast furnace slag to Portland cement was investigated to test the hypothesis that it would reduce the electrochemical potential sufficiently to also reduce the valence of the chromium from the highly soluble Cr^{6+} to the more stable Cr^{3+} .

This work concentrated on the plastic media waste samples P1, P2, P3, and P4 discussed in Phase III, as these had high concentrations of Cr and failed TCLP for Cr. Samples of paint blast media waste were blended and cast with a mixture of Portland cement and granulated blast furnace slag. The cement used in Phase III was replaced with 25% by volume of the blast furnace slag yielding a composition of 75% waste and 25% cement blended with slag. The composition of the blast furnace slag as determined by x-ray fluorescence analysis is given in Table 33. The experimental procedures were similar to those used in Phase III. Samples were cast and allowed to hydrate for 1 or 28 days, as prescribed in the previous section. The pore solutions were expressed and analyzed, and TCLP analyses were performed (see Tables 34 and 35).

Results

The chromium concentration of the expressed pore solution in relation to the $[\text{OH}^-]$ is shown in Figure 12. The different wastes, with different level of contaminants, in the different cement matrices, resulted in different initial $[\text{OH}^-]$. Despite significantly different initial $[\text{OH}^-]$, the partial replacement of the cement with blast furnace slag universally resulted in a decrease in the $[\text{OH}^-]$ and a corresponding decrease in the Cr concentration. For both the 1 and 28 day hydrations the response was the same;

partial replacement of cement by blast furnace slag resulted in a decrease in the $[OH^-]$ and a corresponding decrease in the Cr concentration.

The effect of hydration on the Cr concentration of the expressed pore solutions is shown in Figure 13. The data showed an increase in $[OH^-]$, with an increase in hydration time for all samples with blast furnace slag additions. With the exception of the high-alkali data for samples P1 and P2, the data showed an decrease in the chromium concentration, consistent with the Phase III results. This finding again indicates the occurrence of an unidentified long-term process to yield a decrease in the chromium concentration over time

Samples encapsulated in a mixture of Portland cement and blast furnace slag failed TCLP for Cr (Tables 36 and 37). The addition of blast furnace slag was found to have shifted the final $[OH^-]$ of the TCLP extraction fluid to a slightly lower range of values (Figure 14). However, the impact of blast furnace slag additions is a secondary effect superimposed on the much greater role played by the buffering capacity of the cement matrix on the final $[OH^-]$ of the TCLP extraction fluid. The expressed pore solution results showed a decrease in the Cr concentration with the addition of blast furnace slag. TCLP results showed that although three of the four samples hydrated 1 day and all four samples hydrated 28 days showed a slight decrease in the leachable Cr due to blast furnace slag additions, they all failed TCLP for Cr.

The chemical histories of these samples were quite complex. The waste was mixed with a cement or a cement/slag matrix, allowed to hydrate for 1 or 28 days, and then granulated for TCLP testing. The initial environment of the TCLP extraction was acidic. At some point during the extraction, the buffering capacity was consumed and the pH shifted to highly alkaline conditions. The leachable Cr concentration was then determined. At each step in this process, chemical reactions occurred. Normally in the acid environment of the TCLP test, the blast furnace slag should react with Cr^{6+} and reduce it to the less-soluble Cr^{3+} . It may be possible that this occurred during the initial stages of the TCLP extraction, before the buffering capacity of the acid was consumed. The shift of the TCLP from the initial acidic conditions to highly alkaline conditions had a greater affect on the final $[OH^-]$ and the leachable Cr than the addition of blast furnace slag to the waste form. The leachable chromium concentration measured by the TCLP, with or without blast furnace slag, appeared to be controlled by the final high pH of the extraction solution.

Summary of Phase IV Results

Despite the replacement of the cement with blast slag, the high pH of the cement completely neutralized the acid present in the TCLP test and all samples failed TCLP

for Cr. This had a greater affect on the final $[OH^-]$ and leachable Cr than the addition of blast furnace slag to the waste form. However, the blast furnace slag additions did slightly decrease the $[OH^-]$ and resulted in a corresponding decrease in the Cr concentration in the expressed pore solutions of waste forms hydrated for 28 days. Although this decrease may be due to the reduction of Cr valence by the blast furnace slag, the reaction kinetics appear to be too slow to make this process applicable to Army needs.

Table 24. TCLP results for 10 waste samples for Phase I cement encapsulation study.

Depot	Waste	Stabilization (wt%)	As ppm	Hg ppm	Se ppm	Cr ppm	Cd ppm	Pb ppm	Ag ppm	Ba ppm	Results
ANAD	Coal Slag		BDL	0.089	0.0296	0.497	0.801	BDL	1.5		Pass All
ANAD	Glass Beads		0.049	BDL	0.405	0.245	0.453	BDL	0.6		Pass All
ANAD	Steel		BDL	0.146	BDL	0.121	0.082	BDL	1.5		Pass All
CCAD	Star Blast		0.024	BDL	0.026	0.144	0.084	0.171	0.1	0.1	Pass All
CCAD	Plastic		0.026	BDL	BDL	3.353	0.058	0.479	BDL	0.1	Pass All
ANAD	Mg/Fe Silicates		BDL	BDL	BDL	0.0693	10.051	0.308	0.01	1.7	Fail Cd
ANAD	Mg/Fe Silicates	22%Cem + 11%HO	BDL	BDL	0.017	0.028	BDL	BDL	BDL	0.2	Pass All
ANAD	Alumina		BDL	BDL	BDL	0.602	2.721	0.611	BDL	0.3	Fail Cd
ANAD	Alumina	22%Cem + 11%HO	BDL	BDL ₂	0.023	0.122	BDL	0.019	BDL	0.2	Pass All
SAAD	Sand		BDL	BDL	12.9	1.5	0.1	BDL	0.7		Fail Cr, Cd
SAAD	Sand	22%Cem + 11%HO	BDL	BDL	0.021	6.659	BDL	BDL	BDL	0.2	Fail Cr
SAAD	Sand	22%Cem + 20%HO	BDL	BDL	0.029	7.518	BDL	BDL	BDL	0.2	Fail Cr
SAAD	Sand	33%Cem + 17%HO	BDL	BDL	0.04	4.999	BDL	BDL	BDL	0.4	Fail Cr
SAAD	Plastic		0.094	BDL	0.088	19.6	2.8	0.1	BDL	0.9	Fail Cr, Cd
SAAD	Plastic	22%Cem + 11%HO	BDL	BDL ₂	0.012	13.2	BDL	BDL	BDL	0.2	Fail Cr
SAAD	Plastic	22%Cem + 20%HO	0.04	BDL ₂	0.026	13.2	BDL	BDL	BDL	0.3	Fail Cr
SAAD	Plastic	33%Cem + 17%HO	0.04	BDL ₂	0.025	10.259	BDL	BDL	0.046	0.3	Fail Cr
SAAD	Glass Beads		0.037	BDL	0.0256	0.379	14.8	3.5	BDL	0.3	Fail Cd
SAAD	Glass Beads	22%Cem. + 11%HO	BDL	BDL	0.206	BDL	BDL	BDL	BDL	0.1	Pass All
TCLP Limits			5.0	0.2	1.0	5.0	1.0	5.0	5.0	100.0	

Table 25. Total metal analysis of Army-generated paint blast media waste (ppm).

	Cd	As	Pb	Hg	Ba	Se	Ag	Cr
Plastic 1	172.0	< 11.0	3355.0	<10.0	2812.0	<18.0	<10.0	20557.0
Plastic 2	152.0	<11.0	2909.0	<10.0	2726.0	<18.0	<10.0	18173.0
Plastic 3	39.5	<11.0	570.0	<10.0	467.0	<18.0	<10.0	9192.0
Plastic 4	37.0	<11.0	547.0	<10.0	518.0	<18.0	<10.0	6842.0
Glass 1	457.0	<11.0	129.0	<10.0	10.0	<18.0	<10.0	8.5
Glass 2	45.5	<11.0	332.5	<10.0	18.5	<18.0	<10.0	40.0
Sand 1	15.0	<11.0	77.0	<10.0	893	<18.0	<10.0	815.0
Sand 2	93.5	<11.0	18.0	<10.0	735	<18.0	<10.0	39.0

Table 26. TCLP analysis of Army-generated paint blast media waste (ppm).

Waste	Cd	As	Pb	Hg	Ba	Se	Ag	Cr	Status
Plastic 1	4.90	0.14	<0.066	<0.1	0.65	<0.18	<0.016	43.07	Failed Cd, Cr
Plastic 2	5.15	0.14	<0.066	<0.1	0.74	<0.18	<0.016	44.73	Failed Cd, Cr
Plastic 3	1.35	<0.11	<0.066	<0.1	0.55	<0.18	<0.016	18.01	Failed Cd, Cr
Plastic 4	1.35	<0.11	<0.066	<0.1	0.56	<0.18	<0.016	16.32	Failed Cd, Cr
Glass 1	28.17	<0.11	4.86	<0.1	0.09	<0.18	<0.016	0.16	Failed Cd
Glass 2	1.93	<0.11	0.24	<0.1	0.17	<0.18	<0.016	0.03	Failed Cd
Sand 1	0.62	<0.11	0.18	<0.1	1.03	<0.18	<0.016	0.47	Passed
Sand 2	4.85	<0.11	0.10	<0.1	0.30	<0.18	<0.016	0.10	Failed Cd
TCLP Limit	1.00	5.00	5.00	0.20	100.00	1.00	5.00	5.00	

Table 27. Results of simulated pore solutions for each waste.

Waste	Solution	Time	[OH-] start	[OH-] end	Cd	Pb	Cr	Ba
P1	0.1M	1	0.0993	0.0790	0.02	31.70	92.54	0.05
P1	0.1M	28	0.0998	0.0687	0.029	30.68	89.06	0.03
P1	1M	1	0.993	0.963	0.17	77.29	102.7	0.27
P1	1M	28	0.998	0.945	0.09	84.98	104.5	0.28
P2	0.1M	1	0.0993	0.0818	<0.017	25.69	88.48	0.04
P2	0.1M	28	0.0998	0.0685	0.026	27.62	86.87	0.03
P2	1M	1	0.993	0.960	0.19	74.11	113.8	0.26
P2	1M	28	0.998	0.954	0.11	88.75	106.7	0.30
P3	0.1M	1	0.0993	0.0929	<0.017	8.86	23.22	0.03
P3	0.1M	28	0.0998	0.0887	<0.017	12.49	27.69	0.03
P3	1M	1	0.993	0.980	<0.017	18.01	38.14	0.25
P3	1M	28	0.998	0.980	0.03	21.93	39.95	0.37
P4	0.1M	1	0.0993	0.0935	<0.007	8.91	21.72	<0.03
P4	0.1M	28	0.0998	0.0894	<0.017	13.83	28.00	0.03
P4	1M	1	0.993	0.983	<0.017	18.41	32.00	0.24
P4	1M	28	0.998	0.979	0.04	23.96	36.72	0.39
G5	0.1M	1	0.0993	0.0968	<0.017	2.07	0.129	<0.03
G5	0.1M	28	0.0998	0.0973	<0.017	3.74	0.12	<0.03
G5	1M	1	0.993	0.989	0.31	1.42	0.053	0.05
G5	1M	28	0.989	0.976	0.28	4.71	0.067	0.06
G6	0.1M	1	0.0993	0.0983	<0.017	<0.066	0.032	<0.03
G6	0.1M	28	0.0998	0.0988	<0.017	0.10	0.038	<0.03
G6	1M	1	0.993	0.993	0.28	0.37	0.038	0.04
G6	1M	28	0.989	0.979	0.089	0.60	0.062	<0.03
S7	0.1M	1	0.0993	0.0964	<0.017	0.42	1.258	<0.03
S7	0.1M	28	0.0998	0.0957	<0.017	0.37	1.43	<0.03
S7	1M	1	0.989	0.975	0.019	2.01	1.44	0.29
S7	1M	28	0.993	0.984	<0.017	1.96	1.50	0.13
S8	0.1M	1	0.0993	0.0980	<0.017	0.12	0.144	<0.03
S8	0.1M	28	0.0998	0.0977	<0.017	0.14	0.17	<0.03
S8	1M	1	0.993	0.987	0.18	0.46	0.29	0.09
S8	1M	28	0.989	0.977	0.018	0.48	0.22	0.08

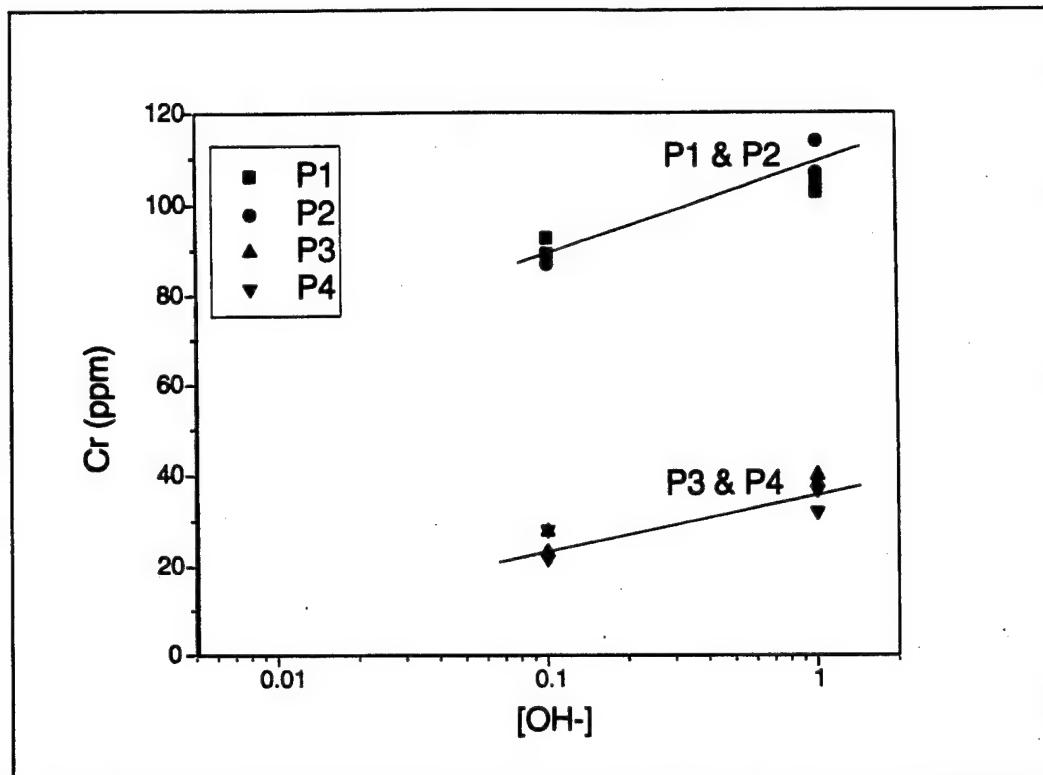


Figure 4. Dependence of chromium concentration on $[OH^-]$ of model pore solutions.

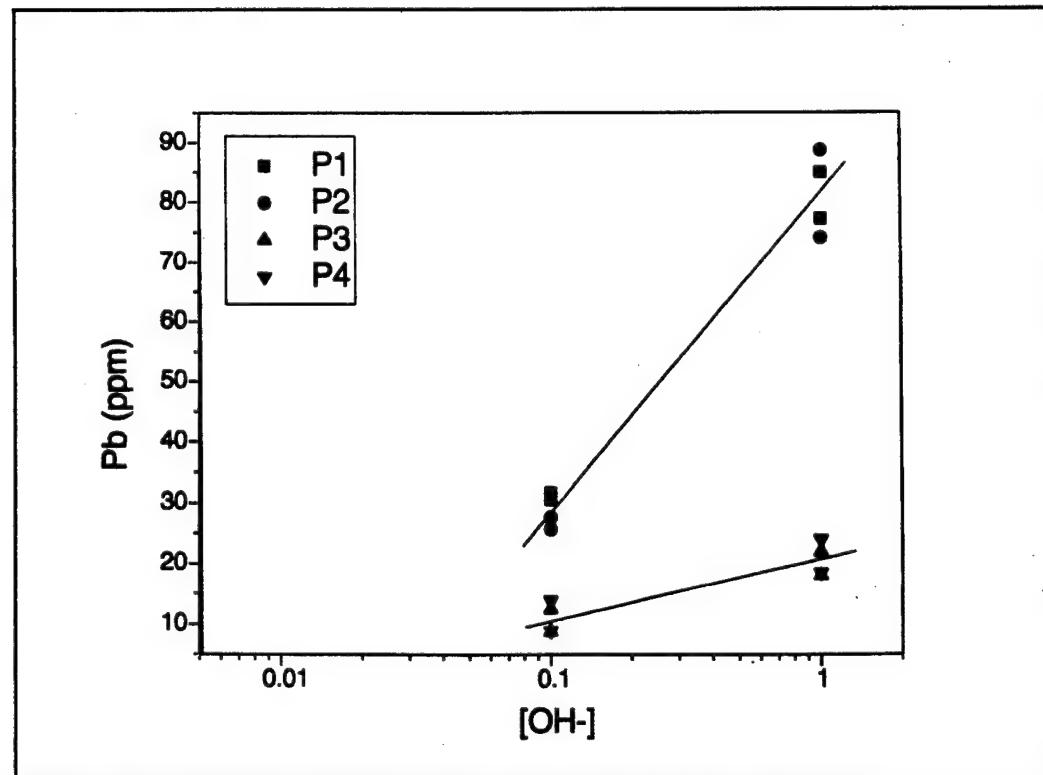


Figure 5. Dependence of lead concentration on $[OH^-]$ of model pore solutions.

Table 28. X-ray fluorescence analysis of low- and high-alkali cements.

Oxide Equivalent	Low Alkali Cement	High Alkali Cement
SiO ₂	24.04	20.45
Al ₂ O ₃	2.58	5.41
Fe ₂ O ₃	0.28	2.00
CaO	68.90	64.21
MgO	1.07	2.72
K ₂ O	0.03	1.07
Na ₂ O	0.14	0.24
TiO ₂	0.13	0.27
P ₂ O ₅	0.10	0.13
MnO	0.02	0.044
SO ₃	2.31	2.93
Totals	99.60	99.47

Table 29. Chemical analysis of expressed pore solutions in low- and high-alkali Portland cement (1-day hydration).

Waste	Cement	Hydration days	Water/Cement (Wt.)	[OH-] end	pH end*	Cd ppm	Pb ppm	Cr ppm	Ba ppm
P1	Low Alk.	1	1.22	0.0160	12.20	0.37	14.9	652	0.58
P1	High Alk.	1	1.21	0.0188	12.27	<0.17	7.7	1310	0.32
P2	Low Alk.	1	1.22	0.0178	12.25	0.30	16.4	612	0.83
P2	High Alk.	1	1.22	0.0200	12.30	<0.17	7.5	1330	<0.30
P3	Low Alk.	1	0.69	0.0728	12.89	<0.17	<0.66	21.5	2.85
P3	High Alk.	1	0.69	0.2390	13.37	<0.17	<0.66	155	2.14
P4	Low Alk.	1	0.69	0.0610	12.79	<0.17	<0.66	11.8	3.27
P4	High Alk.	1	0.69	0.2900	13.46	<0.17	<0.66	87.5	1.32
G5	Low Alk.	1	0.57	0.1115	13.05	<0.17	<0.66	<0.07	1.24
G5	High Alk.	1	0.56	0.5760	13.76	0.189	2.32	0.13	0.45
G6	Low Alk.	1	0.57	0.0820	12.91	<0.17	<0.66	0.07	1.34
G6	High Alk.	1	0.56	0.5212	13.70	<0.17	<0.66	0.40	0.37
S7	Low Alk.	1		0.0751	12.87	<0.17	<0.66	0.36	1.81
S7	High Alk.	1		0.2990	13.48	<0.17	0.78	1.50	1.07
S8	Low Alk.	1		0.0812	12.91	<0.17	<0.66	0.08	1.29
S8	High Alk.	1		0.3558	13.55	<0.17	<0.66	0.16	0.73

*calculated

Table 30. Chemical analysis of expressed pore solutions in low- and high-alkali Portland cement (28-day hydration).

Waste	Cement	Hydration days	Water/Cement (Wt.)	[OH-] end	pH end*	Cd ppm	Pb ppm	Cr ppm	Ba ppm
P1	Low Alk.	28	1.22	0.0180	12.25	0.30	18.1	333	1.05
P1	High Alk.	28	1.21	0.0242	12.38	<0.17	8.46	1080	0.45
P2	Low Alk.	28	1.22	0.0196	12.29	0.29	19.0	263	1.18
P2	High Alk.	28	1.22	0.0252	12.40	<0.17	8.33	1040	0.40
P3	Low Alk.	28	0.69	0.0921	12.96	0.37	1.71	0.40	N/A
P3	High Alk.	28	0.69	0.9572	13.98	<0.17	7.57	49.5	3.16
P4	Low Alk.	28	0.69	0.0773	12.89	<0.17	<0.66	5.26	2.38
P4	High Alk.	28	0.69	0.6730	13.82	<0.17	4.25	30.61	2.71
G5	Low Alk.	28	0.57	0.2520	13.40	<0.17	<0.66	0.25	0.40
G5	High Alk.	28	0.56	0.8620	13.93	<0.17	3.15	1.02	0.46
G6	Low Alk.	28	0.57	0.1916	13.28	<0.17	<0.66	0.13	0.65
G6	High Alk.	28	0.56	0.7745	13.89	<0.17	<0.66	1.09	0.48

*calculated

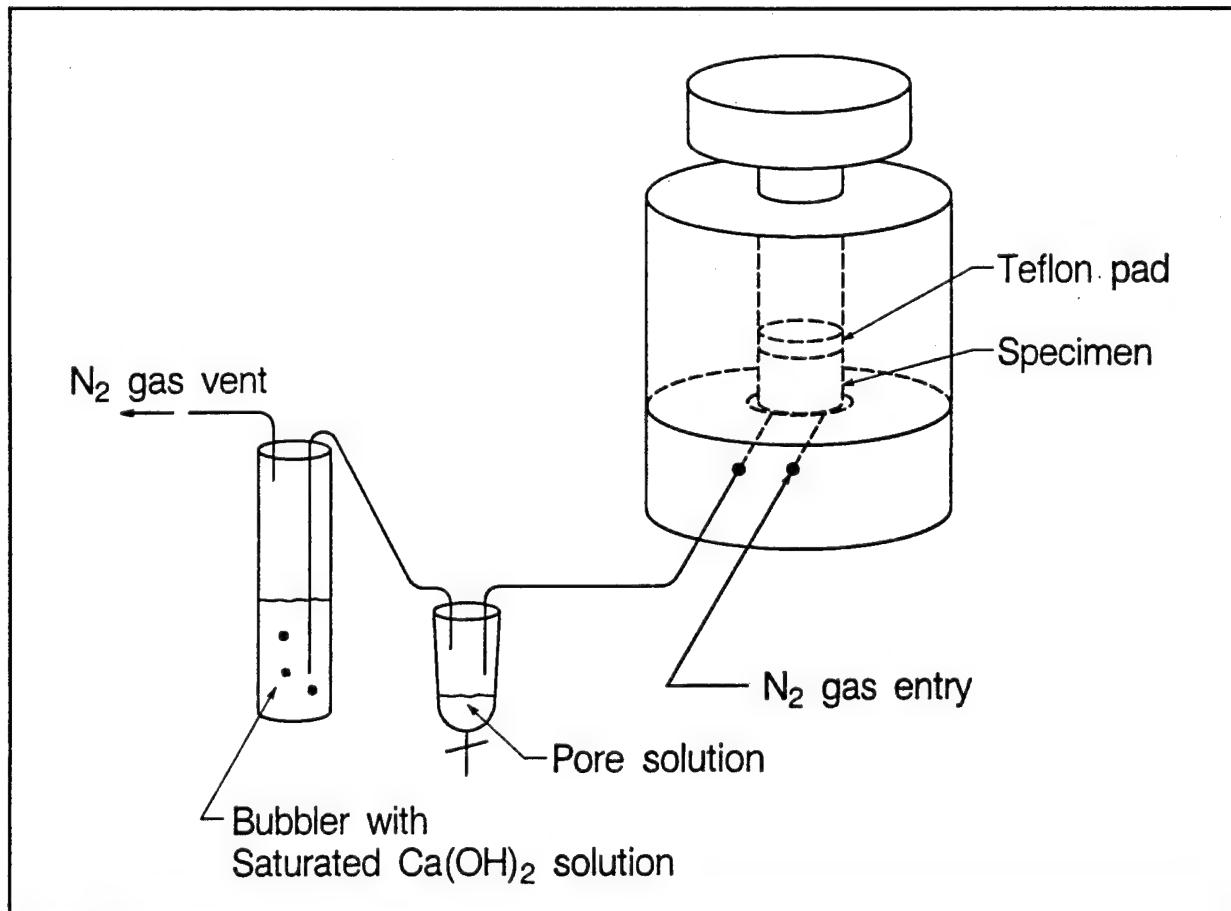


Figure 6. Schematic of pore expression apparatus.

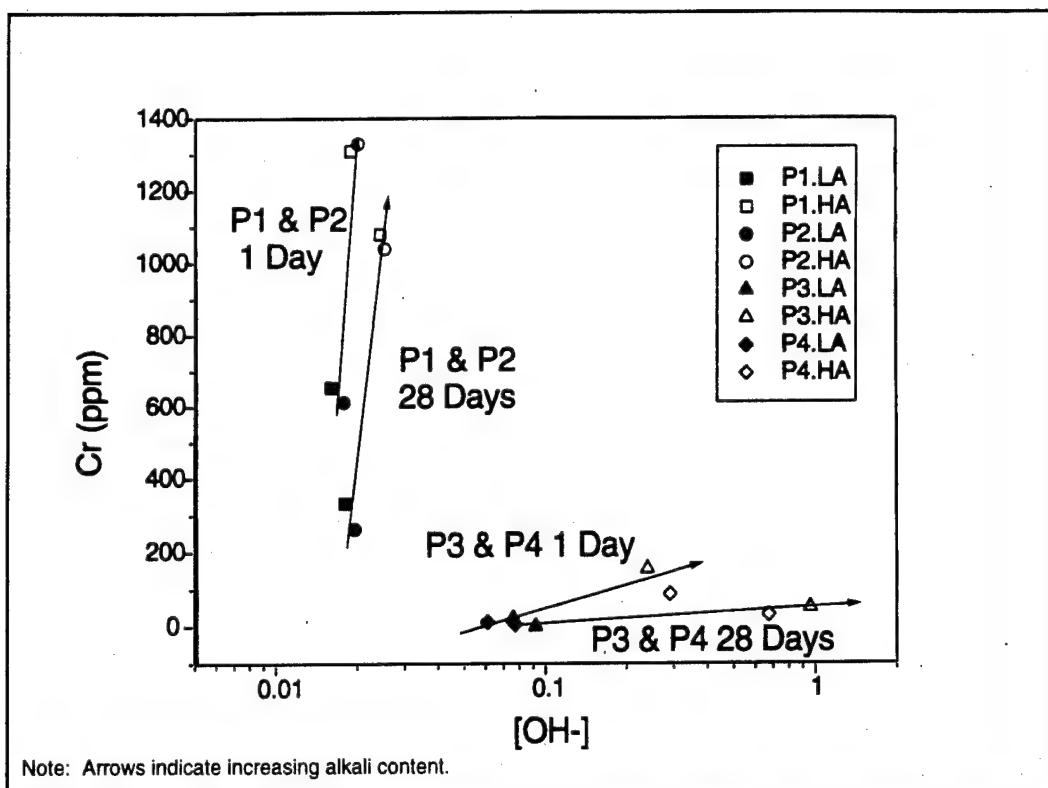


Figure 7. Increase in chromium concentration of expressed pore solutions with alkali content of the expressed pore solution.

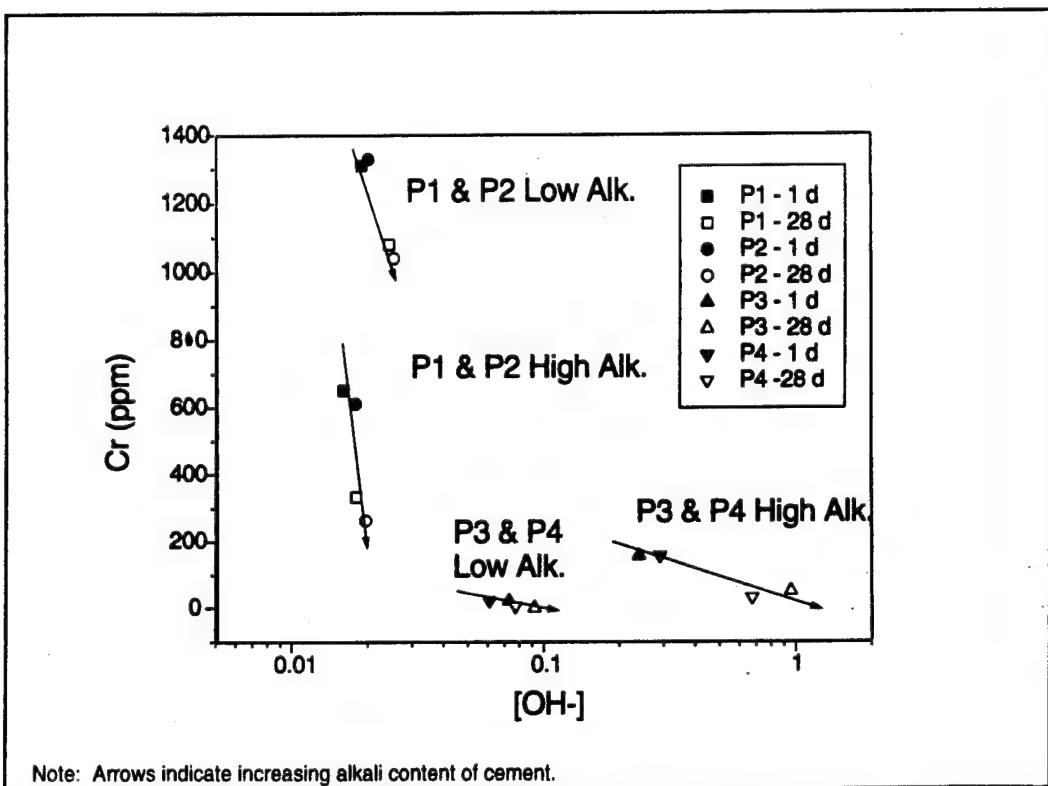


Figure 8. The effect of time on the chromium concentration in expressed pore solution.

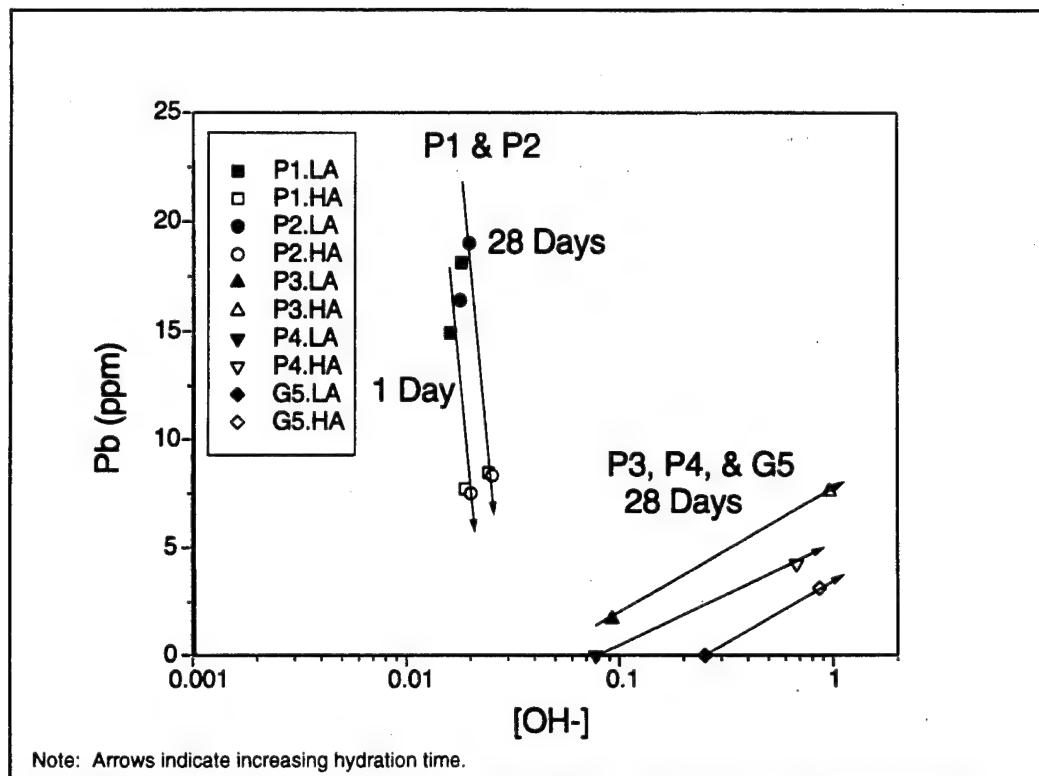


Figure 9. Dependence of lead concentration on the $[OH^-]$ of the expressed pore solutions.

Table 31. Composition of the solid residue retained after pore solution expression.

Waste	Cement	Hydration	pH start	[OH] end	pH end	Cd ppm	Pb ppm	Cr ppm	Ba ppm	TCLP Status
P1	Low Alk.	1	2.92	0.0239	12.37*	<0.017	0.296	19.11	0.43	Failed Cr
P1	High	1	2.92	0.0174	12.24*	<0.017	0.142	18.81	0.41	Failed Cr
P1	Low Alk.	28	2.91	0.0188	12.27*	<0.017	0.18	23.83	0.32	Failed Cr
P1	High	28	2.91	0.0163	12.21*	<0.017	0.13	9.87	0.38	Failed Cr
P2	Low Alk.	1	2.90	0.0261	12.41*	<0.017	0.42	20.47	0.51	Failed Cr
P2	High	1	2.90	0.0207	12.31*	<0.017	0.25	14.96	0.53	Failed Cr
P2	Low Alk.	28	2.91	0.0195	12.29*	<0.017	0.19	24.84	0.37	Failed Cr
P2	High	28	2.91	0.0210	12.32*	<0.017	0.16	10.80	0.52	Failed Cr
G5	Low Alk.	1	2.84		10.50	<0.017	<0.066	<0.007	0.28	Passed
G5	High	1	2.84		11.74	<0.017	<0.066	0.045	0.31	Passed
G5	Low Alk.	28	2.87		10.09	<0.017	<0.066	0.016	0.34	Passed
G5	High	28	2.87		11.70	<0.017	<0.066	0.024	0.42	Passed
G6	Low Alk.	1	2.87		10.05	<0.017	<0.066	0.007	0.31	Passed
G6	High	1	2.87		11.70	<0.017	<0.066	0.063	0.30	Passed
S7	Low Alk.	1	2.86		9.65	<0.017	<0.066	0.142	0.46	Passed
S7	High	1	2.83		11.70	<0.017	<0.066	0.288	0.46	Passed
S8	Low Alk.	1	2.85		10.57	<0.017	<0.066	<0.007	0.36	Passed
S8	High	1	2.85		11.82	<0.017	<0.066	0.032	0.47	Passed
TCLP Limits					1.0	5.0	5.0	100.0		

Table 32. TCLP results for virgin concrete waste samples without pore solution expression.

Waste	Cement	Hydration days	pH start	[OH] end	pH end	Cd ppm	Pb ppm	Cr ppm	Ba ppm	TCLP Status
P1	Low Alk	77	2.90	0.0246	12.39*	<0.017	0.255	22.72	0.39	Failed Cr
P1	High	77	2.90	0.0118	12.07*	<0.017	<0.066	15.07	0.37	Failed Cr
P2	Low Alk.	28	2.91	0.0278	12.44*	<0.017	0.29	16.11	0.43	Failed Cr
P2	High	28	2.91	0.0141	12.14*	<0.017	0.08	15.32	0.36	Failed Cr
TCLP Limit						1.0	5.0	5.0	100.0	

*calculated

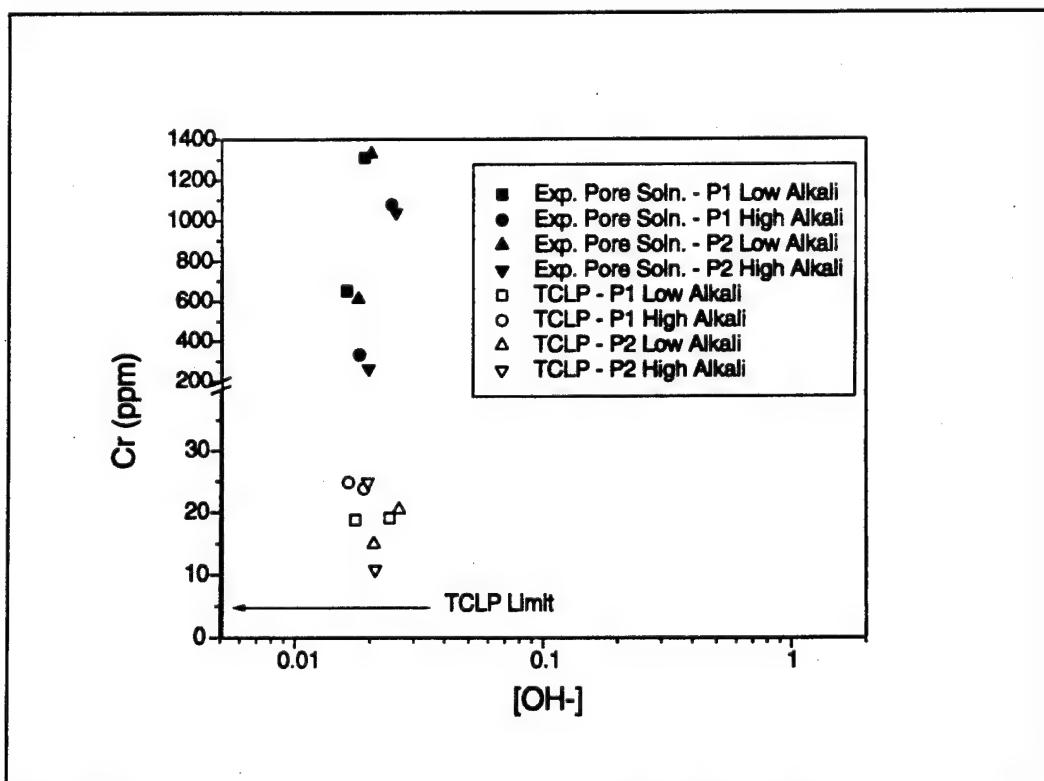
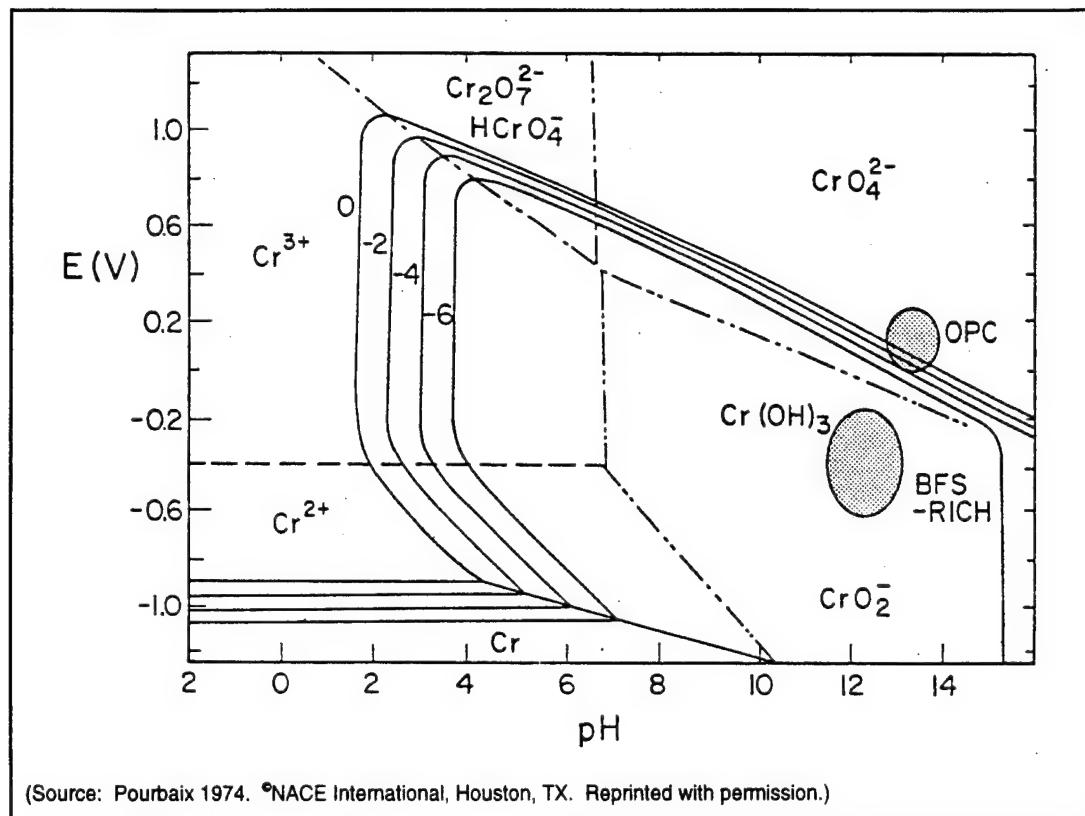


Figure 10. Control of the chromium concentration of both the expressed pore solution and TCLP by the [OH-].



(Source: Pourbaix 1974. ©NACE International, Houston, TX. Reprinted with permission.)

Figure 11. Potential pH for system chromium in waste.

Table 33. X-ray fluorescence analysis of blast furnace slag.

Oxide Equivalent	Blast Furnace Slag
SiO_2	37.55
Al_2O_3	7.45
Fe_2O_3	0.18
CaO	39.07
MgO	11.32
K_2O	0.36
Na_2O	0.30
TiO_2	0.37
P_2O_5	0.01
MnO	0.55
SO_3	2.80
Total	99.96

Table 34. Chemical analysis of expressed pore solutions in high-alkali cement with blast furnace slag (75% waste, 19% cement, 6% slag).

Waste	Cement matrix	Hydration Days	Water/Cement Wt., Vol.	[OH ⁻]	pH	Cr (mg/l)
P1	High Alkali	1	1.21, 3.79	0.0188	12.27*	1310
P1	H.A. + Slag	1	1.21, 3.79	0.0188	12.27*	1210
P1	High Alkali	28	1.21	0.0242	12.38*	1080
P1	H.A. + Slag	28	1.24	0.0227	12.35*	1040
P2	High Alkali	1	1.21, 3.79	0.0200	12.30*	1330
P2	H.A. + Slag	1	1.21, 3.79	0.0171	12.23*	1210
P2	High Alkali	28	1.21	0.0252	12.40*	1040
P2	H.A. + Slag	28	1.24	0.0231	12.36*	1030
P3	High Alkali	1	0.69, 2.15	0.2390	13.38*	155
P3	H.A. + Slag	1	0.71, 2.15	0.1550	13.19*	144
P3	High Alkali	28	0.69	0.9572	13.98*	49.5
P3	H.A. + Slag	28	0.70	0.5486	13.74*	9.22
P4	High Alkali	1	0.69, 2.15	0.2900	13.46*	87.5
P4	H.A. + Slag	1	0.69, 2.15	0.2080	13.32*	76.6
P4	High Alkali	28	0.69	0.6730	13.83*	30.61
P4	H.A. + Slag	28	0.70	0.4578	13.66*	8.37

Table 35. Chemical analysis of expressed pore solutions in low-alkali cement with blast furnace slag (75% waste, 19% cement, 6% slag).

Waste	Cement matrix	Hydration Day	Water/Cement Wt., Vol.	[OH ⁻]	pH	Cr (mg/l)
P1	Low Alkali	1	1.22, 3.79	0.016	12.20*	652
P1	L.A. + Slag	1	1.22, 3.79	0.007	11.84*	227
P1	Low Alkali	28	1.22	0.018	12.25*	333
P1	L.A. + Slag	28	1.22	0.0175	12.24*	459
P2	Low Alkali	1	1.22, 3.79	0.0178	12.25*	612
P2	L.A. + Slag	1	1.22, 3.79	0.010	12.00*	185
P2	Low Alkali	28	1.22	0.0196	12.29*	263
P2	L.A. + Slag	28	1.25	0.0194	12.28*	456
P3	Low Alkali	1	0.69, 2.15	0.0728	12.86*	21.5
P3	L.A. + Slag	1	0.69, 2.15	0.0688	12.84*	20.9
P3	Low Alkali	28	0.69	0.09214	12.96*	N/A
P3	L.A. + Slag	28	0.68	0.08845	12.95*	2.32
P4	Low Alkali	1	0.69, 2.15	0.0610	12.78*	11.8
P4	L.A. + Slag	1	0.71, 2.15	0.0460	12.66*	23.3
P4	Low Alkali	28	0.69	0.07731	12.89*	5.26
P4	L.A. + Slag	28	0.71	0.1214	13.08	3.02

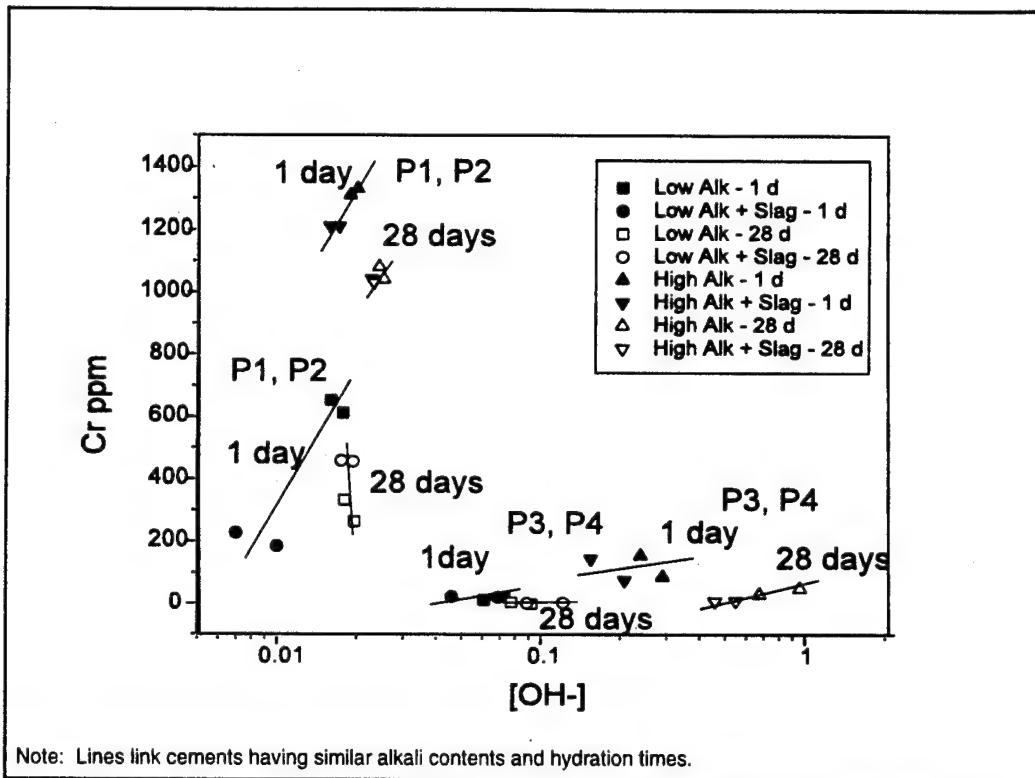


Figure 12. Effects of slag addition on $[\text{OH}^-]$ and chromium concentration of expressed pore solution.

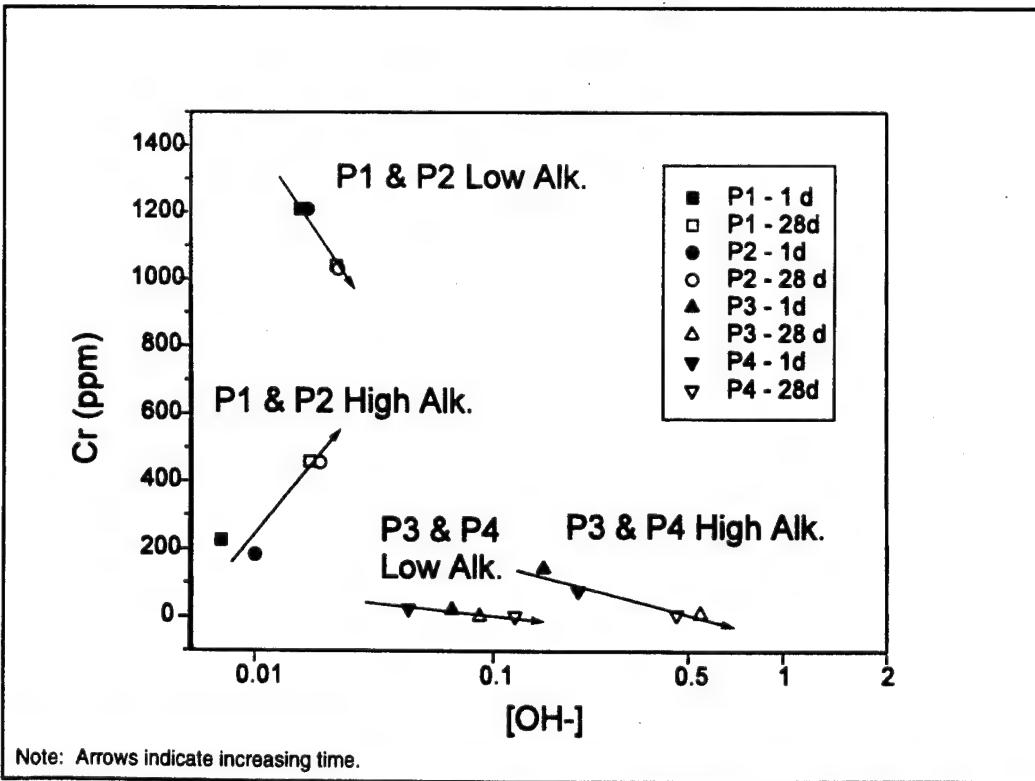


Figure 13. Effects of hydration on $[\text{OH}^-]$ and chromium concentrations of expressed pore solutions.

Table 36. TCLP results for solid residue retained after pore solution expression (75% waste, 19% cement, 6% slag).

Waste	Cement	Slag	Hydration Days	pH Start	[OH ⁻] End	pH End*	Cr (mg/l)	TCLP Status
P1	L.A.	Slag	1	2.92	0.0164	12.2	15.51	Failed Cr
P1	H.A.	Slag	1	2.92	0.0082	11.9	16.00	Failed Cr
P2	L.A.	Slag	1	2.90	0.0175	12.2	16.92	Failed Cr
P2	H.A.	Slag	1	2.90	0.0097	12.0	23.16	Failed Cr
P1	L.A.	Slag	28	2.89	0.0158	12.2	17.38	Failed Cr
P1	H.A.	Slag	28	2.89	0.0059	11.8	7.72	Failed Cr
P2	L.A.	Slag	28	2.91	0.0210	12.3	10.8	Failed Cr
P2	H.A.	Slag	28	2.91	0.0110	12.0	9.00	Failed Cr
TCLP Limit							5.00	

*pH calculated from ionic concentrations

Table 37. TCLP results for virgin concrete waste samples (75% waste, 19% cement, 6% slag).

Waste	Cement	Slag	Hydration Days	pH Start	[OH ⁻] End	pH End*	Cr (mg/l)	TCLP Status
P2	L.A.	No	28	2.92	0.0278	12.4	16.11	Failed Cr
P2	H.A.	No	28	2.92	0.0174	12.1	15.23	Failed Cr
P2	L.A.	Slag	28	2.92	0.0234	12.4	15.99	Failed Cr
P2	H.A.	Slag	28	2.92	0.0094	12.0	19.42	Failed Cr
TCLP Limit							5.00	

*pH calculated from ionic concentrations

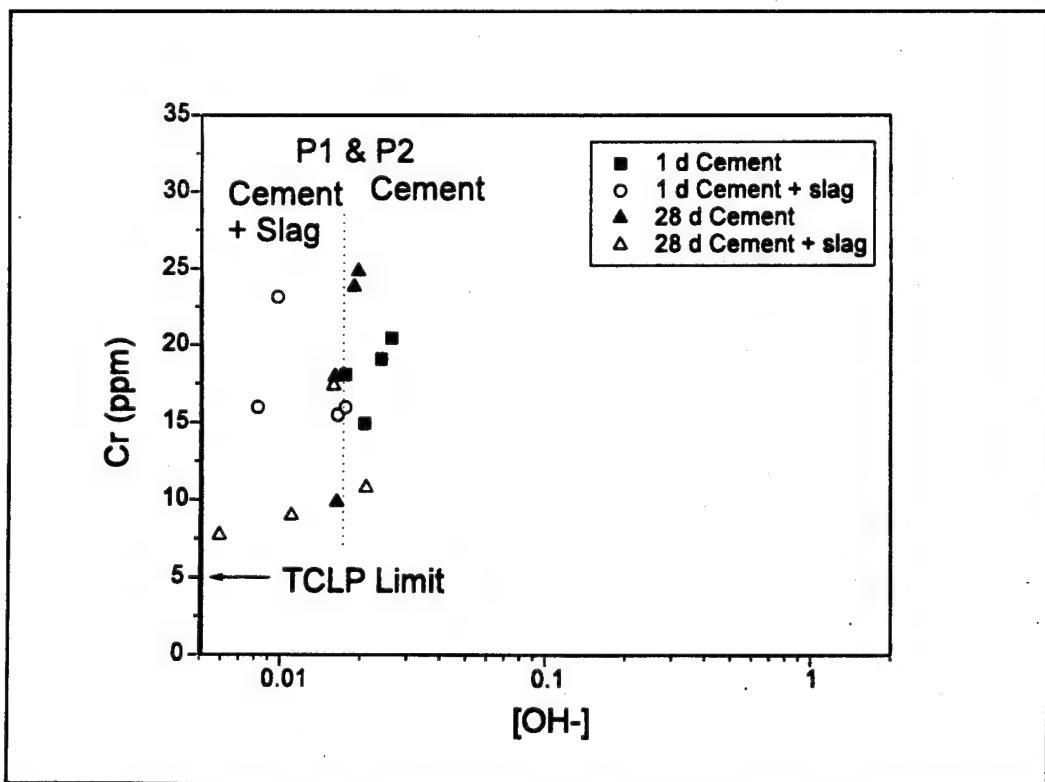


Figure 14. Effects of blast furnace slag additions on final [OH⁻] and chromium concentrations of the TCLP extraction fluid.

9 Chemical Stabilization, Fixation, and Recycling

Background

Red River Army Depot (RRAD) is the Army Center of Technical Excellence (CTX) for chemical stabilization of blast media waste. RRAD has conducted an evaluation of a chemical stabilization and fixation process. The treatment process reduces the level of leachable contaminants, allowing the waste to be classified as non-RCRA, which permits disposal in a Class II landfill. RRAD has received approval from the Texas Natural Resource Conservation Commission to use a Class II landfill for its chemically stabilized paint blast media waste. Chemical stabilization and fixation is not waste-specific.

Process

RRAD contracted for chemical stabilization and fixation services with Perma-Fix Environmental Services Inc., Grand Prairie, TX. The Perma-Fix proprietary two-step process involves chemical reduction followed by fixation. The process is conducted in an onsite mobile unit. The ingredients are properly mixed and poured in containers of 20–30 cu yd.* The containers are covered and stored onsite until analytical data are received. If the waste is classified as non-RCRA, it is disposed of in a Class II landfill.

Between 1 February 1994 and 1 May 1994 RRAD treated and disposed of (onsite) 170,000 kg of paint blast media waste. The treatment costs were estimated to be \$0.33/kg. Cost savings obtained using chemical stabilization, fixation, and disposal in an onsite Class II landfill were estimated at \$240,000. Based on the approximately 340,000 kg of paint blast media used in calendar year 1993, the estimated annual cost savings using the Perma-Fix process at RRAD are \$480,000.

USACERL personnel observed the Perma-Fix process at RRAD in July 1994. Samples of both untreated paint blast media wastes and of wastes treated using the Perma-Fix

* 1 cu yd = 0.7646 m³.

process were obtained and chemically analyzed. In addition to dry blast media waste, a blast media wash sludge is generated at RRAD. This sludge is generated from water jet washing used to remove residual media from vehicles after abrasive blasting. The principal blast media wastes at RRAD consist of sand and garnet.

Chemical analysis indicated that samples of paint blast media waste and blast media wash sludge contained high concentrations of Cr and Pb contaminants (Table 38). All samples of paint blast media waste and one sample of blast media wash sludge failed TCLP for Cd and/or Cr. Samples treated by the Perma-Fix process successfully met TCLP levels for the eight RCRA metals tested. The petroleum hydrocarbon content determined for the blast media wash sludge passed EPA disposal limits (1500 mg/kg) for both the untreated and treated sludge (Table 39).

Discussion

Perma-Fix chemical stabilization and fixation has been found to yield abrasive paint blast media wastes nonleachable by TCLP for the 8 RCRA metals. The use of the Perma-Fix chemical stabilization and fixation process is recommended for the treatment of paint blast media wastes contaminated with the eight RCRA metals. Other commercial chemical stabilization and fixation processes may also be suitable. Additional cost savings can accrue with disposal at an onsite Class II landfill. Paint blast media waste contaminated with hydrocarbons in excesses of EPA disposal limits may require additional treatment prior to disposal.

Table 38. RRAD metals data for the Perma-Fix stabilization and fixation process.

Sample	Test	As (ppm)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	Hg (ppm)	Se (ppm)	Ag (ppm)	Status
Wash Sludge 1	Total Metals	<150	110	<75	880	390	<1.0	<150	<75	
Wash Sludge 2	Total Metals	<150	220	<75	2400	940	<1.0	<150	<75	
Wash Sludge 3	Total Metals	<150	<75	<75	470	250	<1.0	<150	<75	
Wash Sludge 1	TCLP	<0.50	1.2	0.39	0.84	1.3	<0.002	<0.10	<0.50	Passed
Wash Sludge 2	TCLP	<0.50	1.0	2.4	2.8	1.6	<0.002	<0.10	<0.50	Failed Cd
Wash Sludge 3	TCLP	<0.50	<1.0	0.46	<0.50	<0.50	<0.002	<0.10	<0.50	Passed
Treated Wash Sludge A	Total Metals	<150	320	<75	520	250	<1.0	<150	<75	
Treated Wash Sludge B	Total Metals	<150	350	<75	520	270	<1.0	<150	<75	
Treated Wash Sludge A	TCLP	<0.50	<1.0	1.04	<0.50	<0.50	<0.002	<0.10	<0.50	Passed
Treated Wash Sludge B	TCLP	<0.50	<1.0	0.52	<0.50	<0.50	<0.002	<0.10	<0.50	Passed
Blast Waste 1	Total Metals	<150	510	<75	5700	1800	<1.0	<150	<75	
Blast Waste 2	Total Metals	<150	490	<75	6200	1700	<1.0	<150	<75	
Blast Waste 1	TCLP	<0.50	1.3	7	7.9	6	<0.002	<0.10	<0.50	Failed Cd, Cr
Blast Waste 2	TCLP	<0.50	1.3	7.2	8.2	6.1	<0.002	<0.10	<0.50	Failed Cd, Cr
Treated Blast Waste A	Total Metals	<150	730	<75	2900	730	<1.0	<150	<75	
Treated Blast Waste B	Total Metals	<150	<75	<75	<75	<75	<1.0	<150	<75	
Treated Blast Waste A	TCLP	<0.50	<1.0	0.12	<0.50	<0.50	<0.002	<0.10	<0.50	Passed
Treated Blast Waste B	TCLP	<0.50	<1.0	<0.10	4.3	3.1	<0.002	<0.10	<0.50	Passed
	TCLP LIMIT	5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0	

Table 39. RRAD hydrocarbons data for the Perma-Fix stabilization and fixation process.

Sample	Test	Method	H-C's (mg/kg)	Limit (mg/kg)
Wash Sludge 1	Total Hydrocarbon	EPA 418.1	560	1500
Wash Sludge 2	Total Hydrocarbon	EPA 418.1	560	1500
Treated Wash Sludge A	Total Hydrocarbon	EPA 418.1	860	1500
Treated Wash Sludge B	Total Hydrocarbon	EPA 418.1	710	1500

10 Lease and Recycle of Plastic Blast Media

Background

This alternative to separation and treatment involves the leasing of plastic media to the Army depot. The depot uses the blast media in much the same way as purchased media, with the exception that the used media is returned to the manufacturer for reprocessing. It is acceptable for the returned blast media waste to contain paint residues and heavy metal contaminants—even at hazardous concentrations. If 100% of the returned blast media, including paint residue and contaminants, are used or reused as ingredients in an industrial process to make new products, the used media is, according to interpretations of RCRA Section 261.2(e), not considered to be a solid or hazardous waste (Neitzel 1993).

Commercial Processes

Two commercial lease/recycle processes have been identified:

1. U.S. Technology Corp., Canton, OH, uses spent paint blast media as filler in the manufacturing of molded plastic products. All processing is done in the United States.
2. Solidstrip, Inc., Newark, DE, ships spent paint blast media to a processing facility where it is broken down into methylmethacrylate monomer, which in turn is used to make acrylic sheet stock. The processing is done at a facility in Bombay, India.

Personnel at Corpus Christi Army Depot (CCAD) reviewed these commercially available lease/recycle programs and noted the advantages and disadvantages.

Advantages:

- The implementation of lease/recycle agreements is fully compatible with current paint blast operations.
- All types of plastic blast media used at Army depot facilities can be recycled by U.S. Technology Corp.

- The U.S. Technology Corp. process uses the spent plastic blast media in an industrial process to produce cast plastic products. U.S. Technology Corp. assumes liability for the spent media, so the liability of the Army facility is limited.
- The U.S. Technology Corp. plant is located in Canton, OH, and is regulated both by the Federal EPA and the Ohio State EPA.
- The U.S. Technology Corp. process has received approval from the Texas Water Commission for the use at CCAD.

Disadvantages:

- Solidstrip will also recycle thermoset media in a manner similar to U.S. Technology Corp.
- The Solidstrip process accepts only Type V thermoplastic acrylic media. The polymer cracking process used on Type V acrylic media may possibly be classified as a reclamation process such that the original purchaser may retain liability for the waste. The liability issues of this process remain ambiguous.
- The Solidstrip processing facility is located in India, and is not subject to regulation by the Federal EPA.

Pricing of U.S. Technology Corp. plastic blast media lease/recycle program depends on the media type and size purchased, the expected overall volume of the purchases planned during the contract period, the quantity of the shipments both ways, and the shipping distance/freight costs. The annual price for the complete media supply and recycling program ranged between \$2.40/lb to \$2.80/lb.*

Discussion

The use of lease/recycle agreements for plastic media waste is recommended. Reuse of the spent blast media effectively eliminates the waste stream from the Army facility. The Solidstrip process accepts only one type of blast media waste and is less universally applicable than the U.S. Technology Corp. process. The ambiguous liability issues associated with the Solidstrip process must be resolved before the process could be implemented. The U.S. Technology Corp. process—and others like it that use spent media as filler in the subsequent manufacture of molded plastic parts—is a recommended alternative to landfilling.

* 1 lb = 0.4536 kg.

11 Conclusions and Recommendations

Conclusions

In this project seven categories of processing and recycling options for hazardous paint blast waste media were investigated. The work included both laboratory investigations and evaluation of existing technologies including commercially available processes. It is concluded that most of the options studied are not suitable for Army requirements:

- physical separation processes could not effectively isolate hazardous components from plastic media blast wastes
- low-temperature ashing effectively reduced waste volumes but produced the air pollutants phenol and hydrogen cyanide, which could not be filtered out of the combustion gases
- chemical separation through acid extraction and digestion reduced heavy metal concentrations in waste samples by only a small fraction
- biodegradation through a proprietary microbial digestion process reduced the volume of starch-based blast media (ground walnut shells) only, but walnut shells are not a major depaint medium on Army depots; bioremediation in general is complex, and it requires special expertise and equipment not available at most Army depots
- self-encapsulation of plastic media blast waste has been found to be effective only for Type V thermoplastic media, making the technique of limited use on Army depots
- waste stabilized in Portland cement (and Portland cement blended with blast furnace slag) failed the TCLP for chromium.

A commercial chemical stabilization, fixation, and recycling process such as those described in Chapter 9 may be a suitable and cost-effective way for the Army to eliminate some hazardous waste streams from depot depaint operations. When plastic-based hazardous blast media waste is 100% reprocessed and incorporated into a new product, it leaves the waste-disposal regulatory jurisdiction of the Resource Conservation and Recovery Act (RCRA). It appears that some commercial options would relieve the Army of continuing liability for the affected hazardous wastes.

However, each commercial process would have to be reviewed carefully for clarification of liability issues, regulation of the contractor, technical effectiveness, etc.

Recommendations

It is recommended that the Army should not at this time pursue further study of the unsuitable blast media waste treatment options listed above.

It is recommended that Army depot depaint operations consider processing hazardous blast media waste through properly regulated private-sector contractors that provide safe, effective, and economical stabilization, fixation, and recycling processes. Due consideration should include an appropriate legal review of liability and regulatory issues.

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Appendix A: TCLP Metals and Testing Results for Depot Blast Media Wastes

Table A1. Chemical analysis of Sacramento Army Depot blast media waste.

Depot	Sample	ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
SAAD	Plastic	800864	TCLP	Lab A	3/18/93	<0.100	0.369	6.23	189	<0.100	<0.120	<0.170	Failed Cd, Cr	
SAAD	Sand	800865	TCLP	Lab A	3/18/93	<0.100	1.62	0.669	1.04	<0.100	<0.120	<0.170	Passed	
SAAD	Plastic	800864	TCLP	Lab B	2/4/93			5.22	N/A	BDL			Failed Pb	
SAAD	Sand	800865	TCLP	Lab B	2/4/93			0.5	1.49	BDL			Passed	
	LIMIT		TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0	
SAAD	Plastic	800864	Metals	Lab B	5/3/93			191.8	3100	3791.6				

Table A2. Chemical analysis of Anniston Army Depot inorganic blast media waste.

Table A3. Chemical analysis of Anniston Army Depot organic blast media waste.

Depot	Material	Sample ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
ANAD	Walnut	800900	TCLP	Lab A	3/18/93	<0.100	0.291	0.187	1.26	0.185	<0.001	<0.120	<0.170	Passed
ANAD	Walnut	800901	TCLP	Lab A	3/18/93	<0.100	0.285	0.45	1.45	0.281	<0.001	<0.120	<0.170	Passed
ANAD	Walnut	800900	TCLP	Lab B	3/1/94		0.5	1.7	0.7					Passed
ANAD	Walnut	800901	TCLP	Lab B	3/1/94		0.7	1.7	1.1					Passed
	Blank		TCLP	Lab B	3/1/94		BDL	BDL	BDL	BDL				
	LIMIT		TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0	
ANAD	Walnut	800900	Metals	Lab B	5/3/93		3.8		125.7	164.9				
ANAD	Walnut	800901	Metals	Lab B	5/3/93			BDL	BDL	229.2				

Table A4. TCLP analysis of Corpus Christi Army Depot blast media waste.

Depot	Material	Sample ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
CCAD	Glass	800958	TCLP	Lab A	6/30/93	<0.120	0.510	23.3	1.77	0.274	<0.0005	<0.120	<0.170	Failed Cd
CCAD	Plastic 5	800959	TCLP	Lab A	6/30/93	<0.180	2.07	1.40	179.0	<0.120	<0.0005	<0.120	<0.170	Failed Cd, Cr
CCAD	Plastic 2	800960	TCLP	Lab A	6/30/93	<0.120	0.525	0.499	10.7	<0.120	<0.0005	<0.120	<0.170	Failed Cr
CCAD	Glass	800961	TCLP	Lab A	4/13/93	<0.110	0.17	0.72	<0.10	5.05	<0.001	<0.110	<0.39	Failed Pb
CCAD	Plastic 5	800962	TCLP	Lab A	6/30/93	<0.120	1.83	1.17	127.0	<0.120	<0.0005	<0.120	<0.170	Failed Cd, Cr
CCAD	Mix	800963	TCLP	Lab A	6/30/93	<0.120	1.90	0.783	0.649	4.41	<0.0005	<0.120	<0.170	Passed
CCAD	Star Blast	800964	TCLP	Lab A	6/30/93	<0.120	0.790	0.783	2.51	0.146	<0.0005	<0.120	<0.170	Passed
CCAD	Glass	800958	TCLP	Lab B	3/22/93			31.6	2.3	0.7				Failed Cd
CCAD	Plastic 5	800959	TCLP	Lab B	3/22/93			1.8	199.5	0.1				Failed Cd, Cr
CCAD	Plastic 2	800960	TCLP	Lab B	3/22/93			0.6	15.1	0.1				Failed Cr
CCAD	Glass	800961	TCLP	Lab B	3/22/93			1.3	BDL	5.6				Failed Cd, Pb
CCAD	Plastic 5	800962	TCLP	Lab B	3/22/93			1.5	112.1	0.1				Failed Cd, Cr
CCAD	Mix	800963	TCLP	Lab B	3/22/93			27.1	7.5	0.3				Failed Cd, Cr
CCAD	Star Blast	800964	TCLP	Lab B	3/22/93			1.3	4.0	0.2				Failed Cd
	Limit		TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0	

Table A5. Metals analysis of Corpus Christi Army Depot blast media waste.

Depot	Material	Sample ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
CCAD	Glass	800958	Metals	Lab A	6/30/93	<25.0	6.17	472	91.4	13.6	<0.051	<25.0	<2.00	
CCAD	Plastic 5	800959	Metals	Lab A	6/30/93	<25.0	366	115	5370	1990	<0.051	<25.0	<2.00	
CCAD	Plastic 2	800960	Metals	Lab A	6/30/93	<25.0	9.5	10.9	188	8.97	<0.051	<25.0	<2.00	
CCAD	Glass	800961												
CCAD	Plastic 5	800962	Metals	Lab A	6/30/93	<25.0	236	42.9	3320	856	<0.051	<25.0	<2.00	
CCAD	Mix	800963	Metals	Lab A	6/30/93	<25.0	370	16.7	256	888	<0.051	<25.0	<2.00	
CCAD	Star Blast	800964	Metals	Lab A	6/30/93	<25.0	57.8	18.9	194.	300	<0.051	<25.0	<2.00	
CCAD	Glass	800958	Metals	Lab B	5/3/93			464.1	92.2	10.3				
CCAD	Plastic 5	800959	Metals	Lab B	5/3/93			88.2	5172.5	2553.6				
CCAD	Plastic 2	800960	Metals	Lab B	5/3/93			16.7	623.9	48.9				
CCAD	Plastic 2	800960	Metals	Lab B	5/3/93			19.2	730.4	54.3				
CCAD	Glass	800961	Metals	Lab B	5/3/93			20.7	17.9	142.1				
CCAD	Plastic 5	800962	Metals	Lab B	5/3/93			38.1	3495.9	898.8				
CCAD	Mix	800963	Metals	Lab B	5/3/93			6434.2	608.3	68.9				
CCAD	Star Blast	800964	Metals	Lab B	5/3/93			19.4	161.6	268.2				

Table A6. TCLP analysis of Sacramento Army Depot blast media waste.

Depot	Material	Sample ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
SAAD	Plastic	800969	TCLP	Lab A	4/13/93	<0.100	1.03	0.84	6.01	0.23	<0.001	<0.11	<0.39	Failed Cr
SAAD	Sand	800970	TCLP	Lab A	4/13/93	<0.100	1.26	0.75	0.94	0.79	<0.001	<0.11	<0.39	Passed
SAAD	Plastic	800968	TCLP	Lab B	4/16/93			1.5	11.0	BDL				Failed Cd, Cr
SAAD	Plastic	800969	TCLP	Lab B	4/16/93			1.0	8.0	BDL				Failed Cr
SAAD	Sand	800970	TCLP	Lab B	4/16/93			0.7	1.0	0.2				Passed
	BLANK	TCLP	Lab B	4/16/93				BDL	BDL	BDL				
	Limit	TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0		
SAAD	Plastic	800968	Metals	Lab B	4/16/93				39.4	704	727.8			
SAAD	Plastic	800969	Metals	Lab B	4/16/93				20.9	448.3	389.2			
SAAD	Sand	800970	Metals	Lab B	4/16/93				14	79.3	105.3			

Table A7. TCLP analysis results for additional Corpus Christi blast media wastes.

Depot	Material	Sample ID	Sample	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
CCAD	Plastic	1093 A	TCLP	Lab A	11/9/93	<0.500	<10.0	7.01	<0.500	0.675	<0.002	<0.100	<0.500	Failed Cd	
CCAD	Plastic	1093 B	TCLP	Lab A	11/9/93	<0.500	<10.0	0.329	5.07	<0.500	<0.002	<0.100	<0.500	Failed Cr	
	Limit		TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0		
CCAD	Plastic	1093 A	Metals	Lab A	11/9/93	<4.00	6.20	160	3.00	26.0	0.259	<4.00	14.2		
CCAD	Plastic	1093 B	Metals	Lab A	11/9/93	<4.00	<4.00	2.52	41.5	9.36	<0.050	<4.00	<2.00		

Table A8. TCLP and metals test results for Corpus Christi Army Depot blast media waste.

Depot	Material	Sample ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Aq	Status
CCAD	Plastic	Plastic 1	TCLP	Lab C	5/12/94	<0.50	<1.0	1.3	66	<0.50	<0.002	<0.10	<0.50	Failed Cd, Cr
CCAD	Plastic	Plastic 3	TCLP	Lab C	5/25/94	<0.50	1.1	1.9	78	<0.50	<0.002	<0.10	<0.50	Failed Cd, Cr
		Limit	TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0	
CCAD	Plastic	Plastic 1	Metals	Lab C	5/12/94	<2.0	330	74	2900	2900	<1.0	<2.0	<2.0	
CCAD	Plastic	Plastic 3	Metals	Lab C	5/25/94	<2.0	325	60	2700	2800	<1.0	<2.0	<2.0	

Table A9. Chemical analysis results for Tooele Army Depot blast media waste.

Depot	Material	Sample ID	Test	Lab	Date	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Status
TEAD	Plastic	T1	TCLP	Lab C	2/14/94	<5.0	<1.0	1.8	<0.50	<0.50	<0.002	<0.10	<0.5	Failed Cd
TEAD	Plastic	T2	TCLP	Lab C	2/4/94	<5.0	<1.0	1.5	<0.50	<0.50	<0.002	<0.10	<0.5	Failed Cd
TEAD	Ag	T3	TCLP	Lab C	2/14/94	<5.0	1.6	2.9	0.91	0.85	<0.002	<0.10	<0.5	Failed Cd
		Limit	TCLP			5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0	
TEAD	Plastic	T1	Metals	Lab C	2/14/94					220	2200	7000		
TEAD	Plastic	T2	Metals	Lab C	2/14/94					260	2400	7800		
TEAD	Ag	T3	Metals	Lab C	2/14/94					68	320	840		

Table A10. TCLP results for Red River Army Depot blast media waste.

Media	Date	Cd	Cr	Pb	TCLP Status
Steel	Apr.-94	190	BDL	BDL	Failed Cd
Sand/Garnet 1	Apr.-94	9.4	15	BDL	Failed Cd Cr
Sand/Garnet 2	Apr.-94	2.3	2	BDL	Failed Cd
Prefix	Apr.-94	BDL	BDL	BDL	Passed

Appendix B: Detailed Experimental Procedure for Low-Temperature Ashing (LTA)

Determination of Feed Material Mass During LTA

Samples of urea formaldehyde, acrylic, and ground walnut shell blast media were subjected to thermogravimetric (TG) analysis using a Netzsch Model 429 simultaneous thermal analysis instrument. Samples were heated in an air atmosphere with an airflow rate of 100 cc/minute. Samples ranging from 100–180 mg were weighed and heated at a rate of 10 °C per minute until no additional weight loss could be observed. Sample mass loss was expressed as a percentage of sample weight and in terms of percent sample weight/minute (see Figures 1, 2, and 3 in main text, Chapter 4).

Determination of Gaseous Volume Produced During LTA

Experiments were designed to simulate LTA conditions of the three paint blast media samples at 575 °C. Gaseous volumes generated during LTA of the media samples were calculated to estimate the actual gaseous volume that would be produced during waste processing of spent paint blast media. The experimental arrangement included charcoal-filtered high-purity compressed air delivered to the quartz tube housed in a tube furnace capable of achieving temperature of 1100 °C. Gaseous effluent and particulate generated during ashing were passed through a heat exchanger immersed in a water bath for cooling the effluent before mass-flow measurements. Mass-flow measurements were taken with a Sierra Instruments 820 mass-flow meter. Effluent gaseous volume of each sample was determined with a Waugh Controls V/F Integrator (basically, a digital counter). Each combustion experiment was timed with a stopwatch. Integrator count readings were taken at 0.5 minute intervals. Combustion effluent flow rates in liters/minute were calculated from integrated flow volume data and plotted versus time to generate the graphs shown in Figures B1 and B2. The total air volume passed through the quartz tube furnace during combustion experiments was subtracted from the total gaseous volume generated with each media sample to yield the net combustion volume produced from each sample.

Determination of Significant Volatile Organic Compounds (VOCs) Produced

Thermal desorption (TD) gas chromatography mass spectrometry (GC/MS) analyses were conducted on volatile organic compounds (VOCs) produced from LTA of test media and subsequently collected on triple sorbent traps (TSTs). LTA combustion experiments were carried out at air purge flow rates of 2 L/min. VOCs were sampled immediately after smoke was generated and mixed inside a sealed chamber. Triple sorbent traps (76 mm x 4 mm inside diameter) containing Carbotrap C, Carbotrap, and Carbosieve S-III were prepared and conditioned according to the procedure described in Oak Ridge National Laboratory (ORNL) Standard Operating Procedure AC-OP-000-0907. Before sample collection, two blank traps randomly selected from a batch of 30 freshly prepared traps were analyzed by TD and GC/MS to ensure the cleanliness of the traps.

VOCs collected on the triple sorbent traps were thermally desorbed and transferred to GC capillary column for subsequent GC/MS analysis. GC/MS analysis was carried out on an HP 5895 GC/MS system equipped with dual ion source. Typically, a TST was first purged with helium at a flow rate of 200 ml/min for 5 minutes in the same direction of the sampling flow to remove excess absorbed moisture. The trap was then placed in a tube furnace held at 300 °C and purged with helium at a flow rate of 50 ml/min. for 5 minutes in the opposite direction of sampling flow. The desorbed material was transferred directly through a quartz glass liner in the GC injection port to the Cryoloop at the head of the capillary column (60 m x 0.32 mm inside diameter fused-silica capillary column bonded with DB-5 of 1.0 μ m film thickness). The cryoloop was constructed with a 20 cm stainless steel tube (0.04 in. inside diameter [ID], 1/16 in. outside diameter [OD]), and was immersed in a liquid nitrogen bath during the desorbing process. GC oven temperature program was initiated when the liquid nitrogen temperature bath was removed from the cryoloop. The GC oven temperature was held at 50 °C for 5 minutes and then increased to 250 °C at a rate of 10 °C/minutes. Electron impact (EI) mass spectra of the eluate was obtained with an electron energy of 70 eV and emission current of 300 μ A. Source temperature was set at 200 °C. GC injector and transfer line temperatures were set at 280 °C. Mass spectral data was acquired over a mass range or 15-500 amu at a scan rate of 266 amu/sec for all but the TST #29 sample trap (the first trap analyzed). TST #29 (Agrashell) was scanned over a mass range of 30-500 amu, the mass range normally employed for routine analysis in this laboratory. Chamber blank traps which were collected before sample combustion were also analyzed in the same manner as the sample traps. In order to estimate the quantities of major components present in the sample traps, a blank TST was soiled with 0.5 ml of 3.8 μ g/ml d₆-benzene vapor phase standard which was generated using the static dilution method. Quantities of the major components in the sample traps (measured in terms of μ g/L) were estimated based on the response factor of d₆-benzene as an external calibration.

The reconstructed total ion chromatograms from a chamber blank and for the vapor phase samples generated from the combustion of paint blast materials of the ground walnut shell, acrylic, and urea formaldehyde media are presented in Figures B3, B4, and B5. Because of the complex and overly abundant constituents present in each of the vapor phase samples, the effort was focused on the identification of major components. Those components represent a chromatographic area equal to or greater than 1.0% of the total chromatographic area.

The selective ion mode was used to obtain mass chromatograms of m/z 27 and 26 (the two most abundant ions for hydrogen cyanide) to search for the presence of hydrogen cyanide (Figure B6). As shown in Figure B7, mass spectra retrieved from the component eluting at 2.57 min. showed an m/z ratio of 27 ion (100 percent) and an m/z 26 ion (41 percent), which may be related to hydrogen cyanide. This component, representing less than 0.2% of the total chromatographic area, also contained ions generated from water (m/z 18), oxygen (m/z 32, 16), nitrogen (m/z 28), and carbon dioxide (m/z 44). A similar procedure was employed to search for the presence of formaldehyde; none of the early eluting components exhibited the expected characteristic ions generated from formaldehyde.

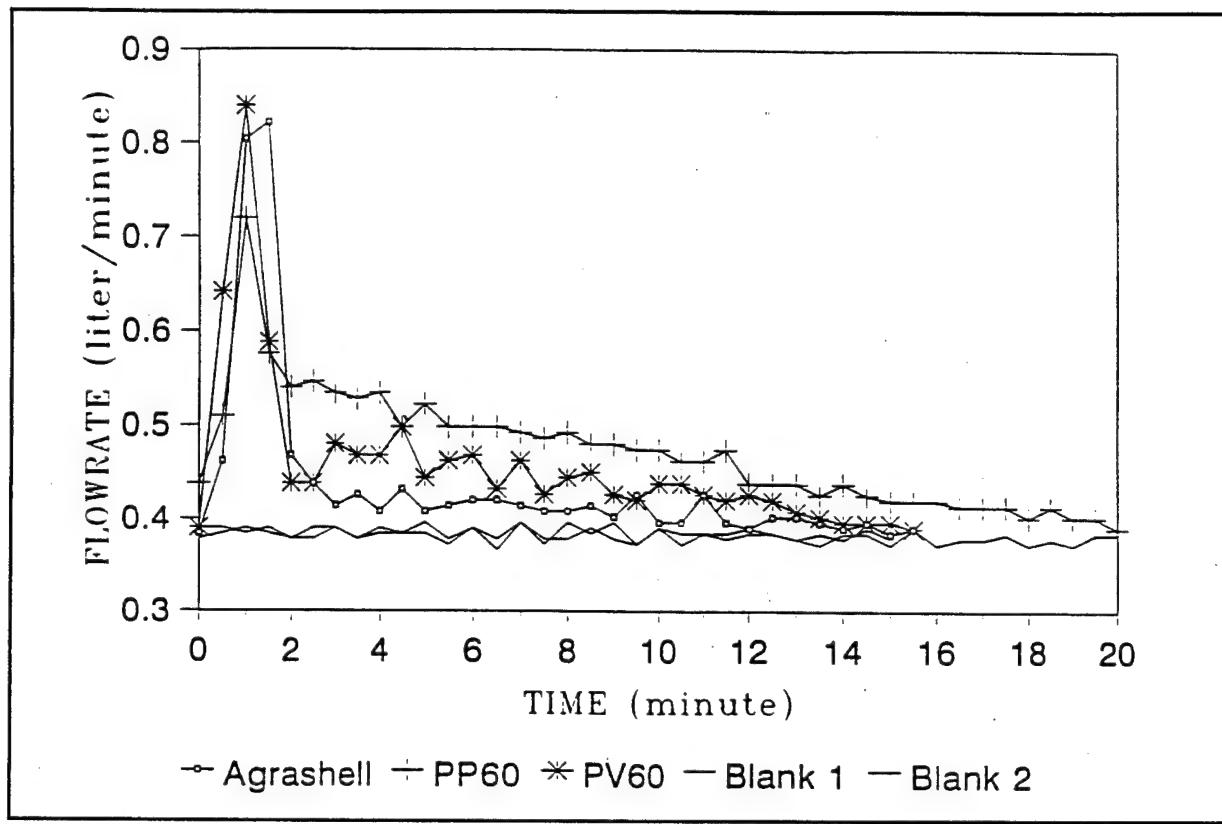


Figure B1. Combustion gas effluent flow rate plotted against time.

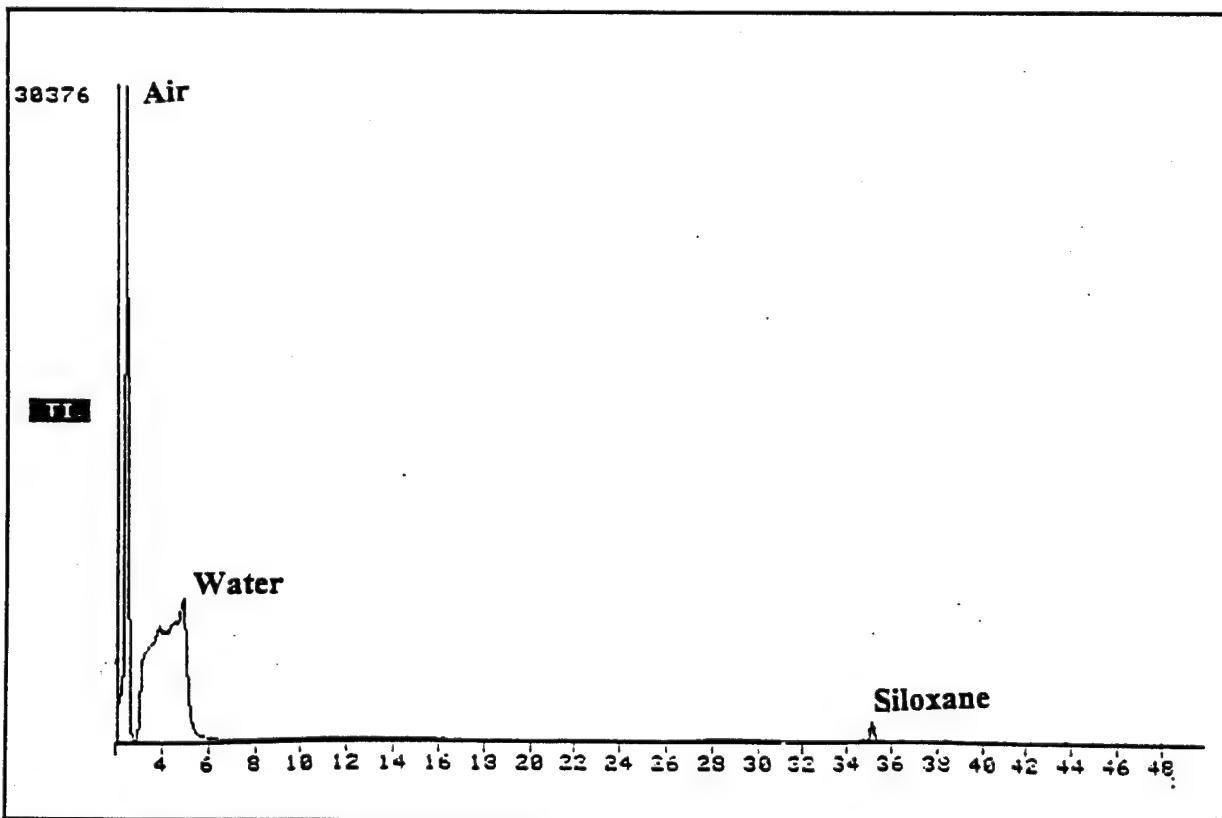


Figure B2. Gas chromatography, chamber blank.

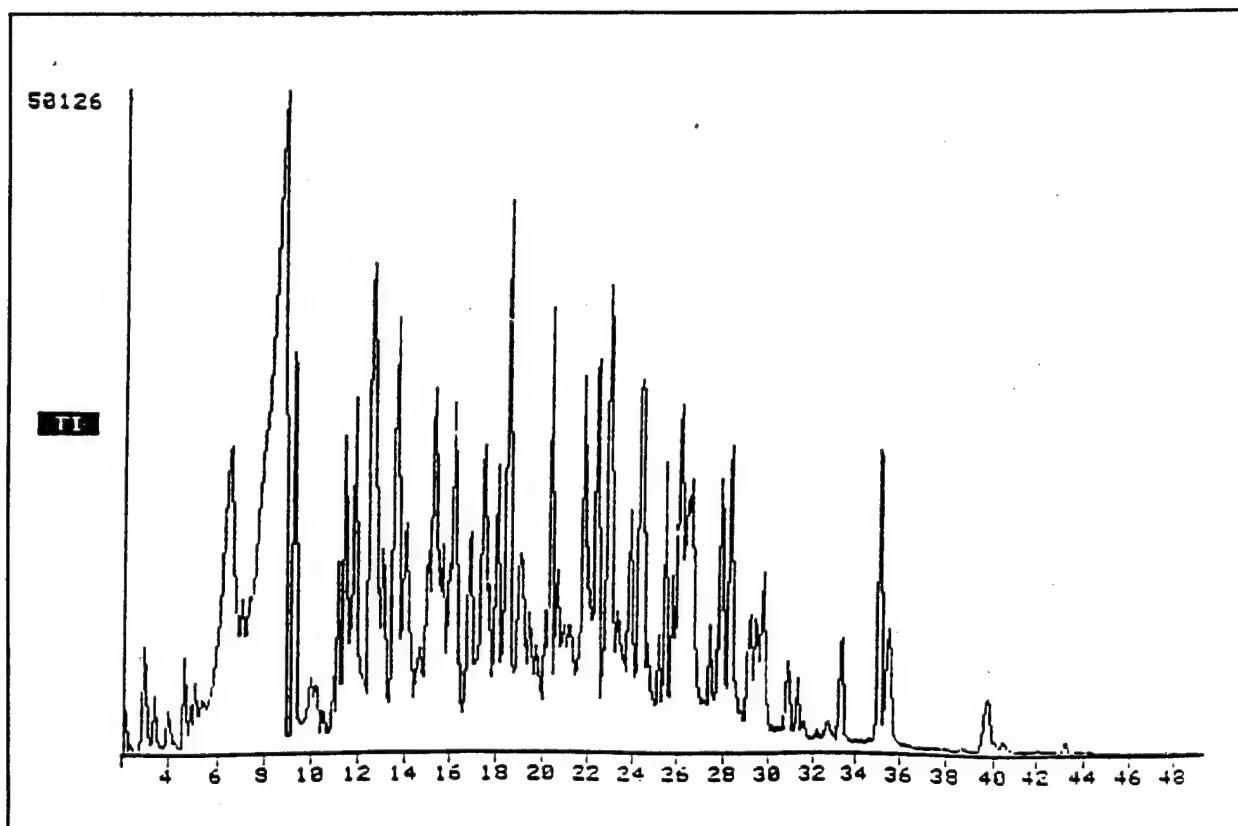


Figure B3. Gas chromatography plot for ground walnut shell blast media treated with LTA.

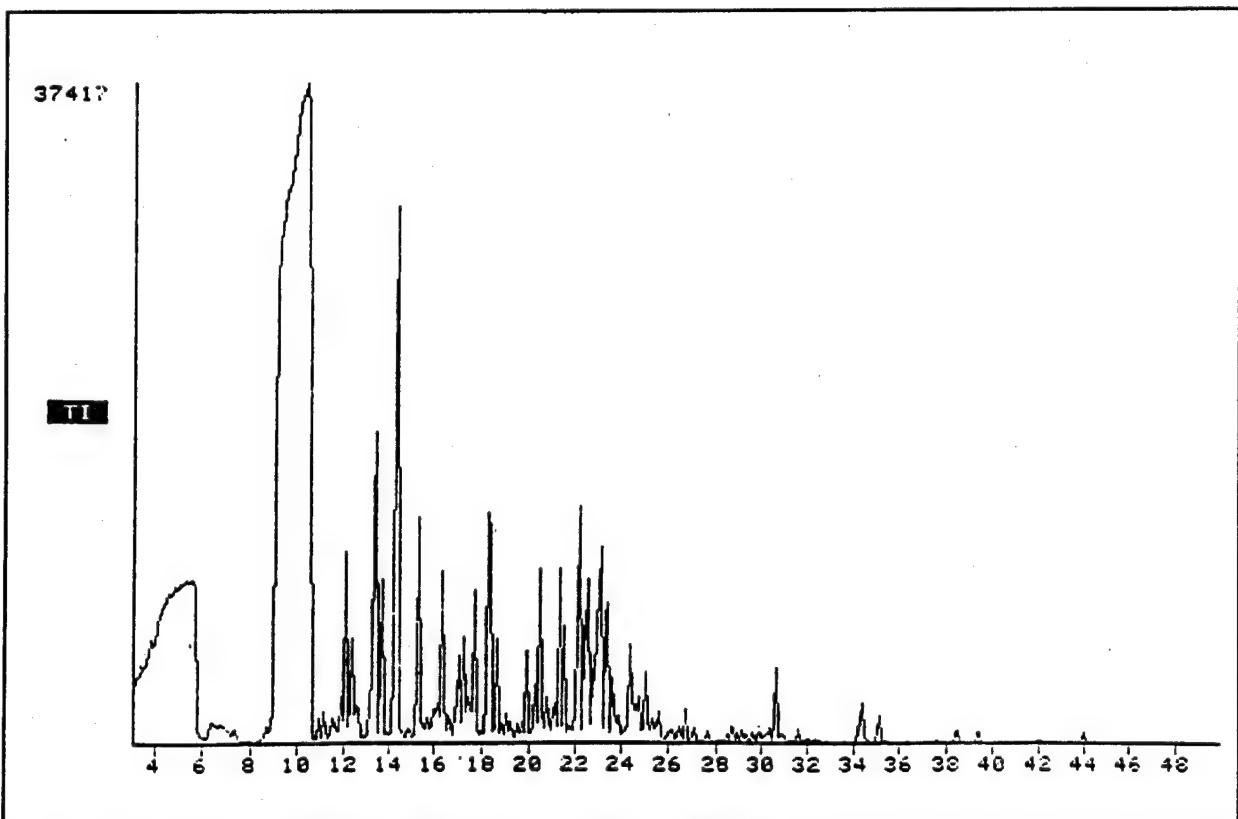


Figure B4. Gas chromatography plot for acrylic blast media treated with LTA.

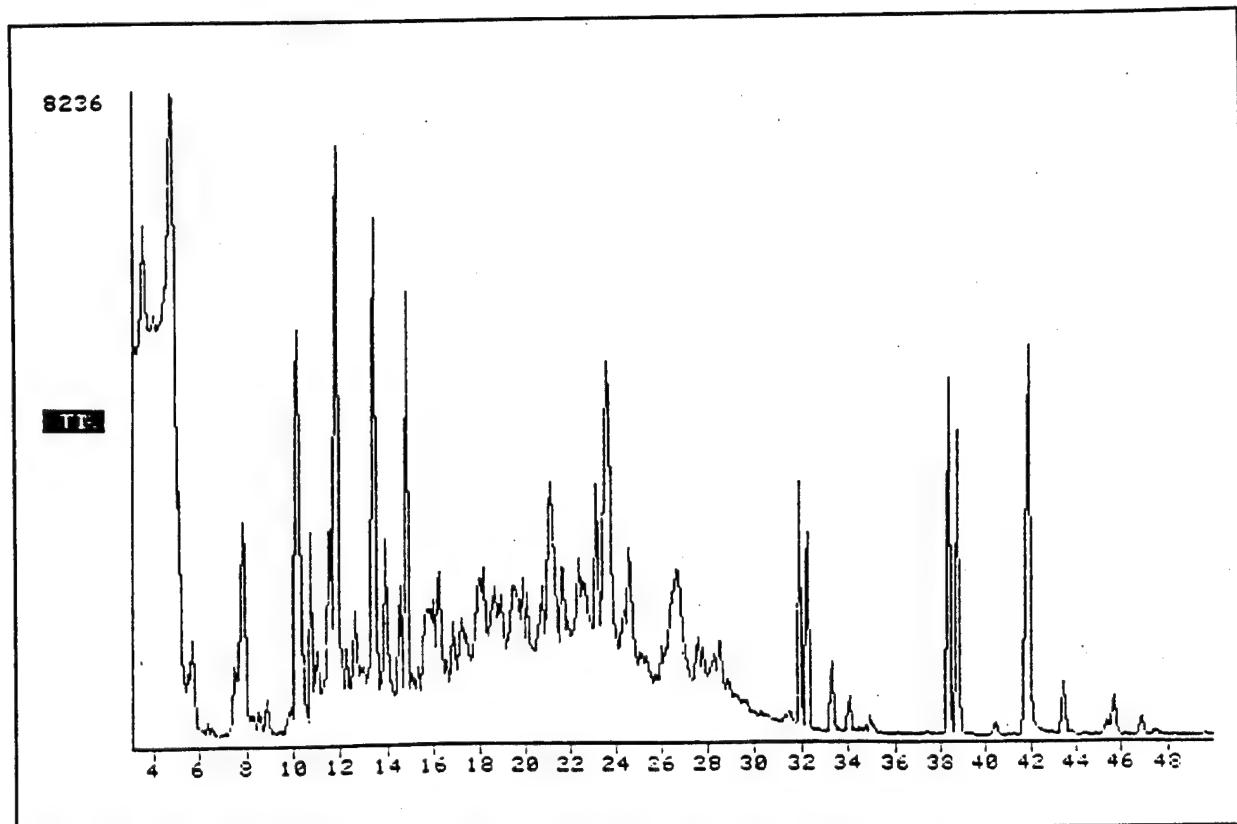


Figure B5. Gas chromatography plot for urea formaldehyde blast media treated with LTA.

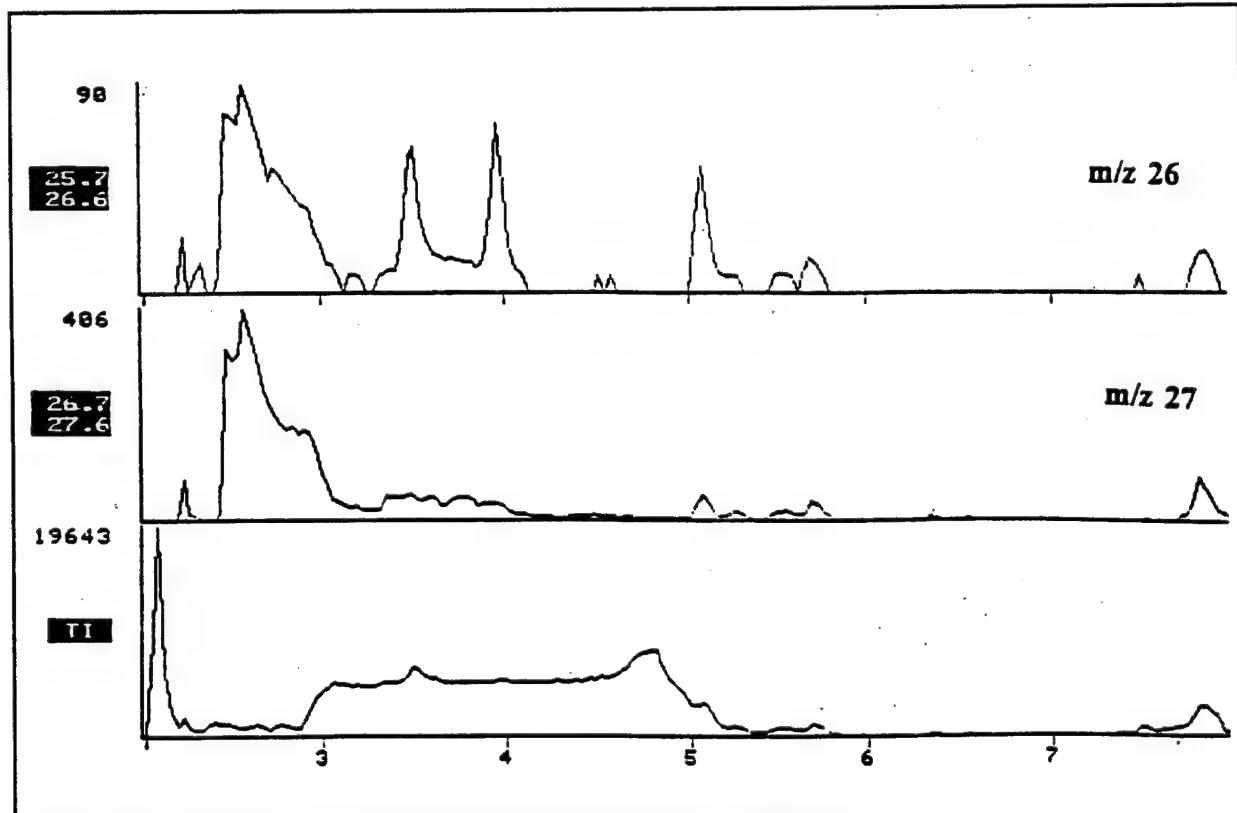


Figure B6. Mass chromatography plot for m/z 26 and m/z 27 treated with LTA.

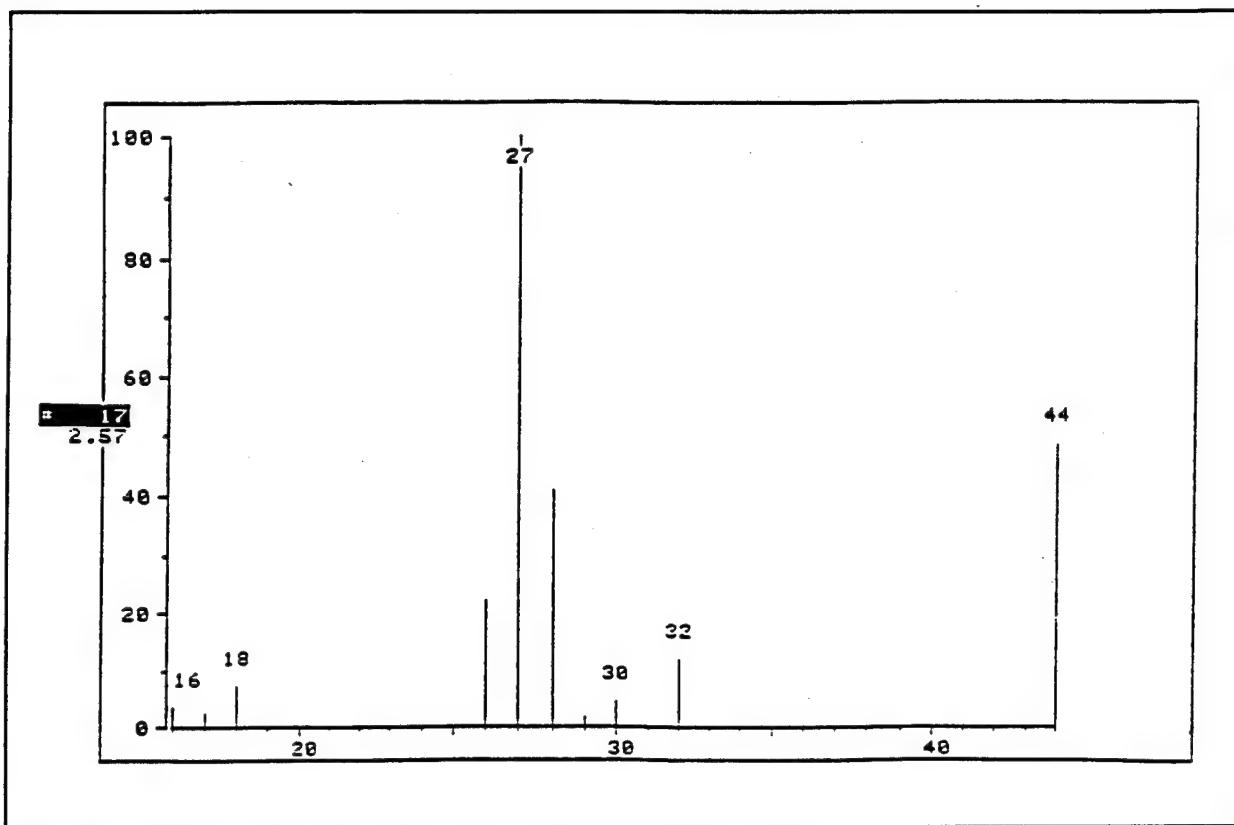


Figure B7. Electron impact mass spectrum for components at 2.57 minutes.

Appendix C: Data for Cement-Based Stabilization Studies

Table C1. Complete chemical results for cement-based stabilization process.

No.	Method	Sample Name	[OH]orph start	[OH]orph end	Pb ppm	Cr ppm	Ca ppm	Al ppm	K ppm	Na ppm	Si ppm	S ppm	Fe ppm	Mg ppm
10	TCLP	blank	4.91	4.88	<0.017	<0.066	<0.007	0.24	0.379					
11	TCLP	Pb3O4-Al2O3	4.89	5.20	0.037	0.068	4.399							
12	TCLP	ZnCrO4-Al2O3	4.91	5.36	0.047	0.30	0.214	Zn 17.57						
13	TCLP	Pb3O4-Al2O3	4.92	5.22	0.028	<0.066	2.406	Zn 42.30						
14	TCLP	ZnCrO4-Al2O3	4.93	5.35	0.034	0.36	0.193	Zn 17.01						
15	TCLP	same#13+0.450mgCr	4.91	5.23	0.027	0.082	3.550	Zn 42.14						
16	TCLP	same#14+5.0mgCr	4.92	5.38	0.034	<0.066	<0.007							
17	TCLP	blank	4.88	4.88	<0.017	6	754	20						
18	TOTAL	HNO3+HCl					8	64						
19	TOTAL	H2SO4					10	740						
20	TOTAL	Al2O3+Pb-LIBO2					8	48	92					
21	TOTAL	Al2O3+Cr-LIBO2												
22	PORE SOLUTION-S	Al2O3+Pb-0.1M1d	0.0902	0.0879	<0.017	2.13	0.009	Zn 9.76						
23	PORE SOLUTION-S	Al2O3+Pb-1M1d	0.8920	0.8910	<0.017	13.86	0.008	Zn 18.79						
24	PORE SOLUTION-S	Al2O3+Cr-0.1M1d	0.0902	0.0877	<0.017	0.72	1.094	Zn 15.20						
25	PORE SOLUTION-S	Al2O3+Cr-1M1d	0.8910	0.8870	<0.017	0.99	1.647	Zn 36.49						
26	PORE SOLUTION-S	1PM-1M1d	0.9953	0.952	0.214	81.44	45.62							
27	PORE SOLUTION-S	3PM-1M1d	0.9953	0.976	<0.017	16.24	12.83							
28	PORE SOLUTION-S	5GB-1M1d	0.9953	0.986	0.343	1.40	0.081							
29	PORE SOLUTION-S	7SB-1M1d	0.9953	0.986	<0.017	2.20	0.613							
30	TOTAL	8SB-LIBO2		86			40	704						
31	TOTAL	8SB-LIBO2					82	38	765					
32	TOTAL	Al2O3-LIBO2					8	51	Zn 313					
33	TOTAL	Al2O3+LIBO2					13	45	Zn 429					
34	TCLP	blank	4.91	4.92	<0.017	<0.066	<0.007							
35	TCLP	SAND-Pb	4.94	4.95	<0.017	2.77	<0.007	<0.03						
36	TCLP	35#+Pb-ICP	4.94	4.95	<0.017	9.33	<0.007							
37	TCLP	SAND-Cr	4.91	4.94	0.031	<0.066	2.40	Zn 28.80						
38	TCLP	37#+Cr+Zn-ICP	4.91	4.94	0.023	<0.066	4.96	Zn 51.46						
39	TCLP	same#13#												
40	TCLP	same#14#												
41	TCLP	39#+Pb-ICP					6.06	4.72						
42	TCLP	40#+Cr-ICP												
43	TCLP	1PM	4.89	5.25	4.90	<0.066	43.07	0.65						
44	TCLP	2PM	4.91	5.25	5.15	<0.066	44.73	0.74						
45	TCLP	3PM	4.92	4.96	1.35	<0.066	18.01	0.55						
46	TCLP	4PM	4.91	4.96	1.35	<0.066	16.32	0.56						
47	TCLP	5GB	4.90	5.00	28.17	4.86	0.16	0.19						
48	TCLP	6GB	4.90	4.93	1.93	0.24	0.03	0.17						
49	TCLP	7SB	4.90	4.98	0.62	0.18	0.47	1.03						
50	TCLP	8SB	4.90	4.93	4.85	0.10	0.10	0.30						
51	TCLP	blank	4.91	4.93	<0.017	0.40	<0.007	<0.03						
52	TCLP	51#+Pb+Cr-ICP			<0.017	4.81	4.52							

No.	METHOD	SAMPLE NAME	OHorPH start	OHorPH end	Cd ppm	Pb ppm	Cr ppm	Ba ppm	Ca ppm	Al ppm	K ppm	Na ppm	Si ppm	S ppm	Fe ppm	Mg ppm
139	TOTAL	5GB-HNO3			4.44	1.20	0.10	0.03								
140	TOTAL	5GB-HNO3+standard			121%	102%	93.3%	98.4%								
141	TOTAL	5GB-HNO3+standard			91.1%	93.5%	93.1%	98.2%								
142	TOTAL	6GB-HNO3			0.52	0.39	0.21	0.14								
143	TOTAL	6GB-HNO3			0.39	0.26	0.13	0.09								
144	TOTAL	143#+standard			92.1%	88.4%	88.3%	91.6%								
145	TOTAL	7SB-HNO3			0.15	0.75	0.36	1.22								
146	TOTAL	7SB-HNO3			0.15	0.79	0.58	1.15								
147	TOTAL	146#+standard			91.3%	89.3%	90.3%	94.4%								
148	ICP-STANDARD	8-element LIBO2-blank					2	<3								
149	TOTAL	5GB-LIBO2					4	9								
150	TOTAL	5GB-LIBO2					13	11								
151	TOTAL	7SB-LIBO2					810	887								
152	TOTAL	7SB-LIBO2					819	899								
153	TOTAL	7SB-LIBO2					45	25								
154	TOTAL	sample144#					35	12								
155	TOTAL	6GB-LIBO2					6812	518								
156	TOTAL	6GB-LIBO2					6865	508								
157	TOTAL	4PM+HNO3-LIBO2					20557	3044								
158	TOTAL	4PM+HNO3-LIBO2					17199	2580								
159	TOTAL	1PM-LIBO2					18470	2780								
160	TOTAL	1PM-LIBO2					18955	2672								
161	TOTAL	2PM-LIBO2					9219	478								
162	TOTAL	2PM-LIBO2					9165	455								
163	TOTAL	3PM-LIBO2			14.5	85	70	121								
164	TOTAL	3PM-LIBO2			15.5	69	60.35	126								
165	TOTAL	7SB-HNO3					689.5	818								
166	TOTAL	7SB-HNO3					726.5	804								
167	TOTAL	7SB-LIBO2 (after 65#)														
168	TOTAL	7SB-LIBO2 (after 66#)														
169	PORE SOLUTION-S	same117#														
170	TCLP	sand	4.93	4.93	<0.017	<0.066	0.008	0.06								
171	TCLP	white cement	2.88	10.45	<0.017	<0.066	<0.007	0.98								
172	STANDARD	8-element-ICP														
173	STANDARD	8-element-ICP														
174	PORE SOLUTION-E	WC-sand	0.0969	<0.17	<0.66	<0.07										
175	PORE SOLUTION-E	WC-sand	0.1182	<0.17	<0.66	<0.07										
176	PORE SOLUTION-E	WC-sand	0.0916	<0.17	<0.66	<0.07										
176A	STANDARD	8-element	0.1115	<0.17	<0.66	<0.07	1.24	431	0.66	261	2174	<1.6	5.78	<0.10	<0.14	
177	PORE SOLUTION-E	5GB-WC1d	0.1189	0.189	2.32	0.13	0.45	102	5.06	18532	2919	35.6	97.2	4.95	<0.14	
178	PORE SOLUTION-E	5GB+HAC1d														
179	PORE SOLUTION-E	6GB-WC1d	0.0820	<0.17	<0.66	0.07	1.34	521	0.33	101	1386	<1.6	0.63	<0.10	<0.14	
180	PORE SOLUTION-E	6GB+HAC1d	0.5212	<0.17	<0.66	0.40	0.37	89.0	5.22	15918	2331	<1.6	55.3	6.58	<0.14	

No.	Method	Sample Name	OHorP start	OHorP end	Cd ppm	Pb ppm	Cr ppm	Ba ppm	Ca ppm	Al ppm	K ppm	Na ppm	Si ppm	S ppm	Fe ppm	Mg ppm	
223	PORE SOLUTION-S	Cu2O-sand-0.1M1d	0.1021	0.0996	<0.017	<0.066	<0.007	Cu1.63	<0.03	<0.007	<0.007	<0.03	<0.03	<0.03	<0.14	<0.14	
224	PORE SOLUTION-S	Cd-sand-0.1M1d	0.1021	0.0995	0.028	<0.066	<0.017	<0.007	Cu8.67	<0.066	<0.007	<0.007	<0.03	<0.03	<0.14	<0.14	
225	PORE SOLUTION-S	Cu2O-sand-1M1d	1.0034	1.0041	<0.017	<0.066	<0.017	<0.007	<0.03	<0.007	<0.007	<0.03	<0.03	<0.03	<0.14	<0.14	
226	PORE SOLUTION-S	Cd-sand-1M1d	1.0034	1.0041	0.265	0.068	<0.017	<0.007	<0.03	<0.007	<0.007	<0.03	<0.03	<0.03	<0.14	<0.14	
227	PORE SOLUTION-E	1PM-WC-1d	0.0160	0.0170	0.37	1.49	652	0.58	4820	1.88	2600	13.9	345	236	20.6	329	
228	PORE SOLUTION-E	1PM-WC-BFS-1d	0.0070	<0.17	6.9	227	1.08	2600	13.9	345	371	17.5	49.7	1.56	1.96	<0.14	
229	PORE SOLUTION-E	1PM-HAC-1d	0.0188	<0.17	7.7	1310	0.32	1700	0.54	6560	848	21.3	1160	1.19	<0.14	<0.14	
230	PORE SOLUTION-E	1PM-HAC-BFS-1d	0.0158	<0.17	<0.66	1210	<0.30	3080	0.65	4980	720	25.0	1380	0.55	<0.14	<0.14	
231	PORE SOLUTION-E	2PM-WC-1d	0.0178	0.30	16.4	612	0.83	4350	1.94	380	353	24.9	66.1	0.84	<0.14	<0.14	
232	PORE SOLUTION-E	2PM-WC-BFS-1d	0.0100	0.21	<0.66	185	1.27	2490	18.2	379	395	19.4	50.7	3.44	<0.14	<0.14	
233	PORE SOLUTION-E	2PM-HAC-1d	0.0200	<0.17	7.5	1330	<0.30	1950	0.67	6760	879	23.5	1270	0.96	<0.14	<0.14	
234	PORE SOLUTION-E	2PM-HAC-BFS-1d	0.0171	<0.17	<0.66	1210	<0.30	2760	0.57	4970	725	23.0	1340	0.45	<0.14	<0.14	
235	PORE SOLUTION-E	3PM-WC-1d	0.0728	<0.17	<0.66	21.5	2.85	987	<0.17	259	714	10.7	57.7	<0.10	<0.14	<0.14	
236	PORE SOLUTION-E	3PM-WC-BFS-1d	0.0688	<0.17	<0.66	20.9	2.59	1390	<0.17	239	546	13.4	43.2	<0.10	<0.14	<0.14	
237	PORE SOLUTION-E	3PM-HAC-1d	0.2390	<0.17	<0.66	155	2.14	173	0.84	13980	1640	22.8	467	0.46	<0.14	<0.14	
238	PORE SOLUTION-E	3PM-HAC-BFS-1d	0.1550	<0.17	<0.66	144	1.93	260	0.25	9230	1140	21.6	311	0.17	<0.14	<0.14	
239	PORE SOLUTION-E	4PM-WC-1d	0.0610	<0.17	<0.66	11.8	3.27	1120	0.20	310	709	8.87	32.5	<0.10	<0.14	<0.14	
240	PORE SOLUTION-E	4PM-WC-BFS-1d	0.0460	<0.17	<0.66	23.3	3.82	939	<0.17	292	627	9.40	49.6	<0.10	<0.14	<0.14	
241	PORE SOLUTION-E	4PM-HAC-1d	0.2900	<0.17	<0.66	87.5	1.32	247	1.55	14070	1630	20.3	275	0.84	<0.14	<0.14	
242	PORE SOLUTION-E	4PM-HAC-BFS-1d	0.2080	<0.17	<0.66	76.6	1.70	333	1.06	10200	1270	16.7	161	0.47	<0.14	<0.14	
243	PORE SOLUTION-S	Pb-sand-0.1M28d	0.1024	0.1009	<0.17	3.90	<0.007	<0.03									
244	PORE SOLUTION-S	Cr-sand-0.1M28d	0.1024	0.1007	<0.17	0.13	4.11										
245	PORE SOLUTION-S	Pb-sand-1M28d	1.0207	1.0117	<0.17	26.94	<0.007	<0.03									
246	PORE SOLUTION-S	Cr-sand-1M28d	1.0207	1.0117	<0.17	0.21	2.96	<0.03									
247	PORE SOLUTION-E	5GB-WC-1d	0.0824	<0.17	<0.66	0.15	0.98	247	<0.17	175	1879	14.3	10.9	<0.10	<0.14	<0.14	
248	PORE SOLUTION-E	5GB-HAC-1d	0.5078	<0.17	2.96	0.28	0.58	119	5.70	17059	2683	50.2	61.1	3.99	<0.14	<0.14	
249	PORE SOLUTION-E	6GB-WC1d	0.0766	<0.17	<0.66	0.17	2.01	645	0.65	81.5	1242	7.83	<1.9	<0.10	<0.14	<0.14	
250	PORE SOLUTION-E	6GB-HAC-1d	0.4560	<0.17	<0.66	1.40	0.50	117	4.49	15963	2130	16.5	49.7	4.71	<0.14	<0.14	
251	PORE SOLUTION-E	1PM-WC-28d	0.0180	0.30	18.1	933	1.05	6400	1.63	479	68.6	61.0	0.96	<0.14	<0.14	<0.14	
252	PORE SOLUTION-E	1PM-WC-BFS-28d	0.0175	0.29	11.5	459	0.72	6700	1.11	453	427	70.2	128	0.67	<0.14	<0.14	
253	PORE SOLUTION-E	1PM-HAC-28d	0.0242	<0.17	8.46	1080	0.46	5680	1.10	7080	910	83.9	802	2.25	0.56	0.56	
254	PORE SOLUTION-E	1PM-HAC-BFS-28d	0.0227	<0.17	5.90	1040	0.31	6590	0.59	5190	739	79.6	950	1.23	0.22	0.22	
255	PORE SOLUTION-E	2PM-WC-28d	0.0196	0.29	19.0	263	1.18	6060	1.38	474	468	71.9	62.3	0.88	<0.14	<0.14	
256	PORE SOLUTION-S	C1-BFS-0.1M1d	0.1024	0.0975	<0.17	0.10	4.33	<0.03									
257	PORE SOLUTION-S	C1-BFS-1M1d	1.0163	0.9975	<0.17	<0.066	3.35	0.13									
258	PORE SOLUTION-E	2PM-WC-BFS-28d	0.0194	<0.17	13.8	456	0.77	7030	1.21	461	474	75.7	142	0.77	<0.14	<0.14	
259	PORE SOLUTION-E	2PM-HAC-28d	0.0252	<0.17	8.33	1040	0.40	5680	0.76	6830	872	80.7	864	2.07	0.30	0.30	
260	PORE SOLUTION-E	2PM-HAC-BFS-28d	0.0231	<0.17	6.94	1030	0.38	6760	0.77	5180	757	81.6	922	1.51	0.38	0.38	
261	PORE SOLUTION-E	3PM-WC-28d	0.0921	0.37	1.71	0.40		15.0	0.30	<15.8	15.7	2.57	<1.9	0.70	7.56	7.56	
262	PORE SOLUTION-E	3PM-WC-BFS-28d	0.0885	<0.17	<0.66	2.32	2.58	696	0.54	1377	2524	30.0	250	0.47	<0.14	<0.14	
263	PORE SOLUTION-E	2PM-WC-HighBFS-1d	0.0131	<0.17	2.46	770	0.45	3759	0.55	213	273	17.6	354	0.11	0.70	0.70	
264	PORE SOLUTION-E	2PM-HAC-HighBFS-1d	0.0131	<0.17	2.32	845	0.19	3797	0.44	1254	402	19.4	770	0.17	0.80	0.80	
265	PORE SOLUTION-E	3PM-HAC-28d	0.9572	<0.17	7.57	49.5	3.16	124	124	46030	8137	132	327	5.06	<0.14	<0.14	

No.	METHOD	SAMPLE NAME	OHorPH start	[OHorPH end]	Cd ppm	Pb ppm	Cr ppm	Ba ppm	Ca ppm	Al ppm	K ppm	Na ppm	Si ppm	S ppm	Fe ppm	Mg ppm
266	PORE SOLUTION-E	3PM-HAC-BFS-28d	0.5486	<0.17	1.18	9.22	3.86	176	5.14	25595	5649	85.4	427	2.92	<0.14	
267	PORE SOLUTION-E	4PM-WC-28d	0.0773	<0.17	<0.66	5.26	2.38	812	0.34	786	2511	26.3	38.9	<0.10	<0.14	
268	PORE SOLUTION-E	4PM-WC-BFS-28d	0.1214	<0.17	<0.66	3.02	8.51	692	0.71	2849	4859	44.1	472	<0.10	<0.14	
269	PORE SOLUTION-E	4PM-HAC-28d	0.6730	<0.17	4.25	30.61	2.71	121	4.26	33414	5994	92.4	248	2.81	<0.14	
270	PORE SOLUTION-E	4PM-HAC-BFS-28d	0.4578	<0.17	0.91	8.37	2.63	175	4.14	21161	4478	62.6	375	1.74	<0.14	
271	PORE SOLUTION-S	Cd-sand-0.1M28d	0.1024	0.0998	0.037	<0.066	0.084	<0.03								
272	PORE SOLUTION-S	Cu2O-sand-0.1M28d	0.1024	0.1002	<0.017	<0.066	0.014	Cu0.33								
273	TCLP	2PM-WC-BFS-28d-NOT-E	2.92	0.0234	0.33	15.99	0.47	2913	0.19	13.09	17.87	1.70	78.6	0.01	0.08	
274	TCLP	2PM-HAC-BFS-28d-NOT-E	2.92	0.0094	<0.017	0.079	19.42	0.40	2480	0.28	118.1	24.58	3.72	154	0.03	0.19
275	PORE SOLUTION-E	5GB-WC-28d	0.2520	<0.17	<0.66	0.25	0.40	141	1.49	521	6549	116	67.9	0.22	<0.14	
276	PORE SOLUTION-E	5GB-HAC-28d	0.8620	<0.17	3.15	1.02	0.46	67.3	9.26	23862	7115	480	244	4.79	<0.14	
277	PORE SOLUTION-E	6GB-WC-28d	0.1916	<0.17	<0.66	0.13	0.65	215	1.13	438	4227	41.2	20.8	<0.10	<0.14	
278	PORE SOLUTION-E	6GB-HAC-28d	0.7745	<0.17	<0.66	1.09	0.48	58.3	8.55	23049	4783	28.2	162	7.20	<0.14	
279	PORE SOLUTION-S	Cd-sand-1M28d	1.0035	1.0079	0.347	<0.006	<0.007									
280	PORE SOLUTION-S	Cu2O-sand-1M28d	1.0035	1.0022	<0.017	<0.066	0.011	Cu32.15								
281	TCLP	Pb-BFS	2.86	9.49	<0.017	<0.066	<0.007	0.33								
282	TCLP	PORE SOLUTION-S	2.86	9.48	<0.017	<0.066	<0.007	0.32								
283	TCLP	PORE SOLUTION-S	Cr(metal)-0.01M1d													
284	TCLP	PORE SOLUTION-S	Cr(metal)-0.1M1d													
285	PORE SOLUTION-S	Cr(metal)-1M1d	0.1021	0.0994	<0.017	<0.066	<0.007	0.06								
286	PORE SOLUTION-S	Pb-BFS-0.1M1d	1.0213	1.0041	<0.017	<0.066	<0.007	0.14								
287	PORE SOLUTION-S	Pb-BFS-1M1d	1.0213	0.0994	0.09	2.50	959	0.48	8950	1.7	448	355	262	451	0.20	
288	PORE SOLUTION-E	2PM-WC-HighBFS-28d	0.0155	0.0134	0.04	1.71	960	0.34	8940	1.3	1609	471	148	814	0.40	
289	PORE SOLUTION-E	2PM-HAC-HighBFS-28d	0.0121	0.0112	<0.017	<0.066	9.73	0.38	1942	0.15	15.23	14.03	15.88	67.65	0.01	52.21
290	TCLP	2PM-WC-HighBFS-1d	2.91	0.0012	<0.017	<0.066	8.38	0.41	2082	0.14	29.74	15.67	12.86	75.74	<0.01	72.59
291	TCLP	2PM-HAC-HighBFS-1d	2.91	0.0012	<0.017	<0.066	8.38	0.41	2082	0.14	29.74	15.67	12.86	75.74	<0.01	72.59
292	TCLP	2PM-WC-28d-NOT-E	2.91	0.0278	<0.017	0.29	16.11	0.43	2623	0.29	12.08	19.12	3.43	86.1	0.01	0.07
293	TCLP	2PM-HAC-28d-NOT-E	2.91	0.0141	<0.017	0.08	15.32	0.36	2452	0.29	166.2	27.54	5.28	177.2	0.01	0.14
294	TCLP	2PM-WC-28d	2.91	0.0195	<0.017	0.19	24.84	0.37	2432	0.46	4.92	10.89	3.33	84.7	<0.01	0.06
295	TCLP	2PM-WC-BFS-28d	2.91	0.0160	<0.017	0.14	17.98	0.39	2347	0.44	6.58	11.45	2.81	82.6	<0.01	0.07
296	TCLP	2PM-HAC-28d	2.91	0.0210	<0.017	0.16	10.80	0.52	2408	0.20	59.55	14.61	3.31	93.93	<0.01	0.06
297	TCLP	2PM-HAC-BFS-28d	2.91	0.0110	<0.017	0.08	9.00	0.39	2291	0.73	40.35	12.56	4.10	140.5	<0.01	0.09
298	PORE SOLUTION-S	Cr-BFS-0.1M28d	0.1017	0.0969	<0.017	<0.066	2.42	0.07								
299	PORE SOLUTION-S	Cr-BFS-1M28d	0.1017	0.0984	<0.017	<0.066	2.65	0.15								
300	TCLP	2PM-WC-HighBFS-28d	2.91	0.0009	<0.017	<0.066	5.89	0.39	1945	0.12	14.12	14.85	13.97	67.51	0.02	83.15
301	TCLP	2PM-HAC-HighBFS-28d	2.91	0.0009	<0.017	<0.066	6.28	0.40	1848	0.13	23.71	13.61	16.37	74.39	0.02	175.2
302	TCLP	1PM-WC-28d	2.91	0.0188	<0.017	0.18	23.83	0.32	2486	0.53	4.54	8.56	3.00	95.30	<0.01	0.58
303	TCLP	1PM+HAC-28d	2.91	0.0163	<0.017	0.13	9.87	0.38	2450	0.19	52.37	11.13	4.00	151.2	<0.01	0.26
304	TCLP	1PM+WC-BFS-28d	2.89	0.0158	<0.017	0.14	17.38	0.36	2385	0.52	6.39	10.31	3.35	90.31	0.01	0.19
305	TCLP	1PM+HAC-BFS-28d	2.89	0.0059	<0.017	<0.066	7.72	0.36	2240	0.39	47.11	12.27	6.87	156.0	0.01	0.59
306	PORE SOLUTION-S	Pb-BFS-0.1M28d	0.1021	0.0978	<0.017	0.098	<0.007	0.07								
307	PORE SOLUTION-S	Pb-BFS-0.1M28d	1.0213	0.9998	<0.017	<0.066	<0.007	0.15								
308	TCLP	0.1%2Cr04-BFS(MIX)	2.91	9.50										<0.007		

No.	Method	Sample Name	OH _n Ph start	OH _n Ph end	Cd ppm	Pb ppm	Cr ppm	Ba ppm	Ca ppm	Al ppm	K ppm	Na ppm	Si ppm	S ppm	Fe ppm	Mg ppm
309	TCLP	1%ZnCrO ₄ -BFS	2.91	9.46			3.41									
310	TCLP	2%ZnCrO ₄ -BFS(MIX)	2.91	9.50	0.0261	<0.017	0.42	20.47	0.51	2607	0.38	19.07	17.84	9.01	99.18	<0.01
311	TCLP	2PM-WC-1d	2.90	0.0207	<0.017	0.25	14.96	0.53	2491	0.30	74.23	18.66	9.31	120.4	<0.01	0.10
312	TCLP	2PM-HAC-1d	2.90	0.0175	<0.017	0.19	16.92	0.43	2307	0.58	14.74	14.74	3.73	89.55	<0.01	0.10
313	TCLP	2PM-WC-BFS-1d	2.90	0.0097	<0.017	0.14	11.94	0.41	2318	0.76	56.29	16.60	4.51	164.1	<0.01	0.10
314	TCLP	2PM-HAC-BFS-1d	2.90													
315		Cr-standard-BFS														
316	TCLP	Cd-sand	4.92	4.97	52.18	<0.066	<0.007	Cu23.53								
317	TCLP	Cu20-sand	4.89	4.91	0.021	<0.066										
318	TCLP	1%ZnCrO ₄ -BFS(MIX)	2.91	9.44	0.0246	<0.017	0.255	22.72	0.39	2579	0.36	11.55	17.43	13.71	73.26	0.01
319	TCLP	1PM-WC-NOT-E	2.90	0.0118	<0.017	<0.066	15.07	0.37	2389	0.42	158.6	25.20	11.39	159.5	0.01	0.20
320	TCLP	1PM-HAC-NOT-E	2.90	0.0118	<0.017	0.162	15.94	0.39	2444	0.43	13.09	17.14	6.84	83.4	0.01	0.10
321	TCLP	1PM-WC-BFS-NOT-E	2.91	0.0179	<0.017	<0.017	16.54	0.37	2364	0.60	127.8	24.02	31.75	172.2	0.02	0.20
322	TCLP	1PM-HAC-BFS-NOT-E	2.91	0.0072	<0.017	<0.066	19.11	0.43	2472	0.35	9.59	14.47	2.90	83.20	<0.01	0.10
323	TCLP	1PM-WC-1d	2.92	0.0239	<0.017	0.296	18.81	0.43	2399	0.18	113.6	20.08	3.76	158.0	<0.01	0.10
324	TCLP	1PM-HAC-1d	2.92	0.0174	<0.017	0.142	18.81	0.41	2399	0.54	10.00	13.98	2.56	85.54	<0.01	0.10
325	TCLP	1PM-WC-BFS-1d	2.92	0.0164	<0.017	0.168	15.51	0.37	2325	0.52	91.55	18.79	4.68	168.9	0.01	0.20
326	TCLP	1PM-HAC-BFS-1d	2.91	0.0082	<0.017	0.066	16.00	0.37	2270	0.35	676	71.6	5788	12624	19.8	10144
327	PORE SOLUTION-E	RRAD PERMAFIX D 7d			0.0062	<0.17	0.09	0.10	0.35						3.3	2.0
328	TCLP	RRAD PERMAFIX D 7d	2.92	6.49	0.030	<0.066	0.052	0.38	2251	5.54	42.93	66.97	22.65	774.4	84.35	68.18
329	PORE SOLUTION-E	RRAD PERMAFIX C 28d			0.0063	<0.17	0.15	0.23	0.30	5079	11981	75.0	7384	2.8	7.0	

Abbreviations and Acronyms

amu	atomic mass unit
CFC	chlorofluorocarbon
CTX	Center for Technical Excellence
DESCOM	U.S. Army Depot Systems Command
DI	deionized
EI	electron impact
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectroscopy
HCN	hydrogen cyanide
ID	inside diameter
LiBO ₂	lithium metaborate
LTA	low-temperature ashing
M	molar concentration
MPa	megapascals
MSDS	Material Safety Data Sheet
m/z	mass/atomic number
OD	outside diameter
ORNL	Oak Ridge National Laboratory
PMB	plastic media blasting
RCRA	Resource Conservation and Recovery Act
RRAD	Red River Army Depot
TCLP	Toxicity Characteristic Leaching Procedure
TD	thermal desorption
TG	thermogravimetric (analysis)
TST	triple sorbent trap
USACERL	U.S. Army Construction Engineering Research Laboratories
USAEC	U.S. Army Environmental Center
VOC	volatile organic compound

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